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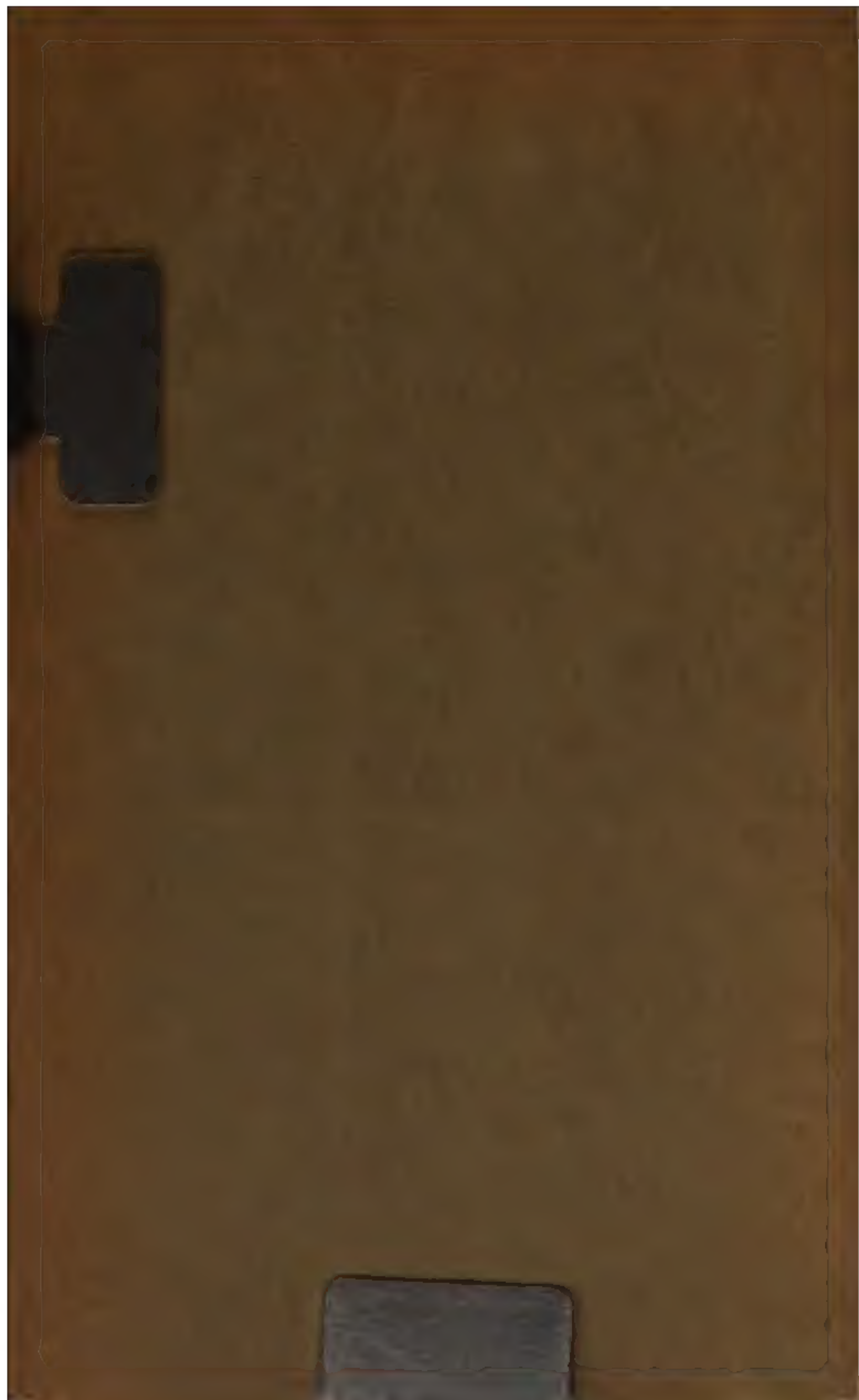
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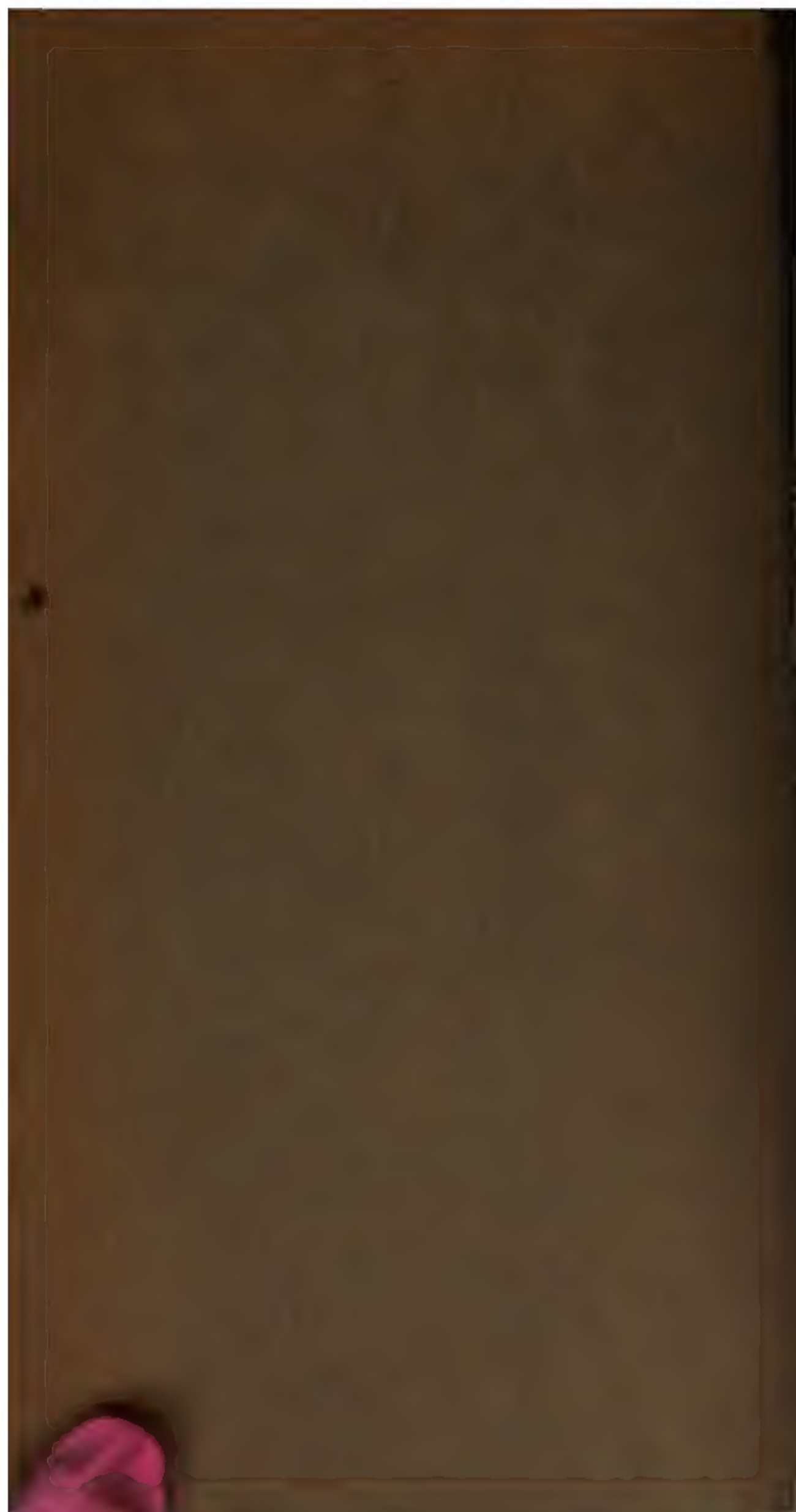
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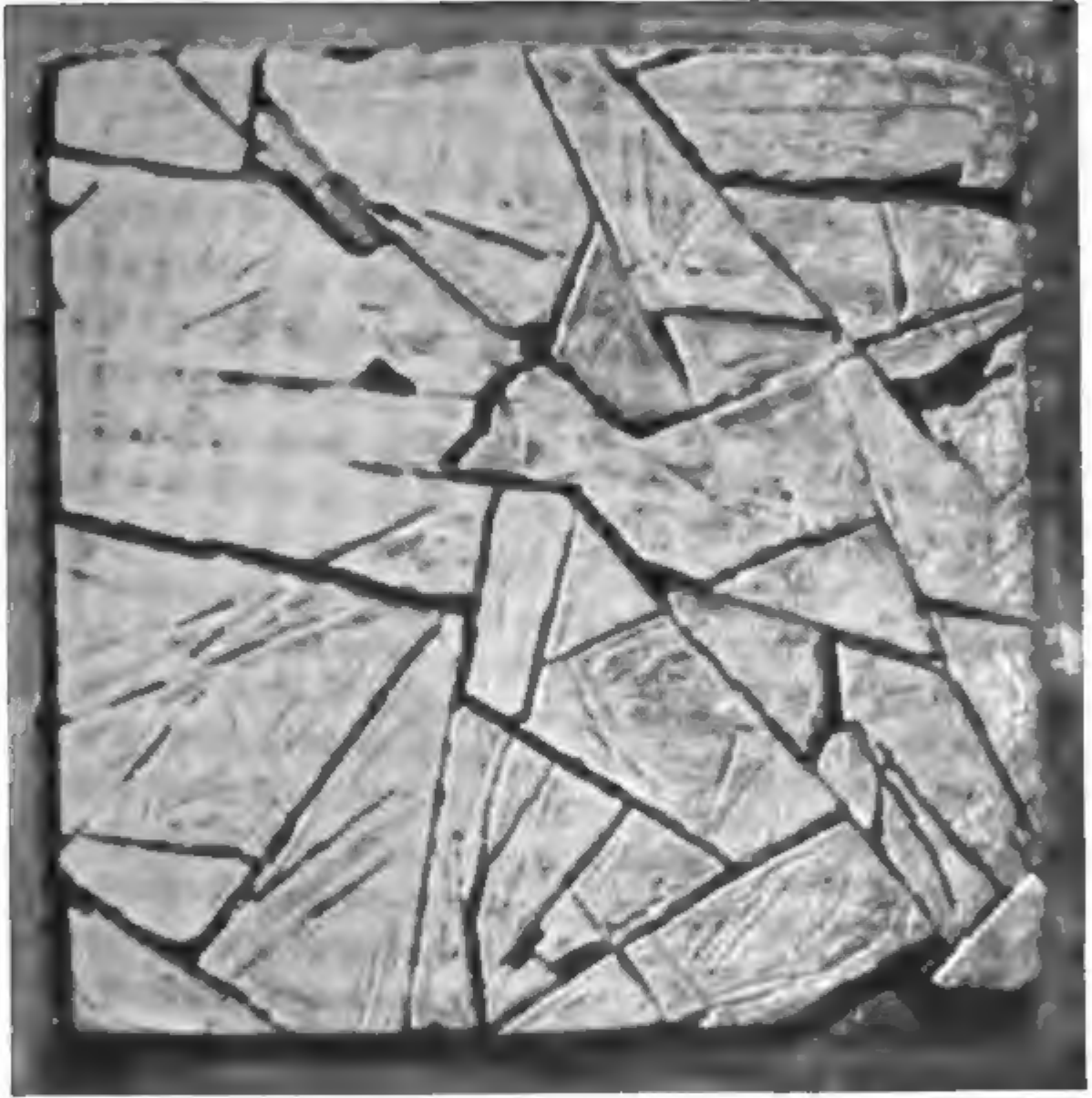








**THE ANALYSIS OF STEEL-WORKS MATERIALS**



**SPIEGELKIESEL.**—Enlarged from micro-section,  $1\frac{1}{2}$  inches square, polished and mounted in 1864 by Dr. H. C. Sorby, F.R.S.

THE ANALYSIS  
OF  
TEEL-WORKS MATERIALS

BY  
HARRY BREARLEY  
" "  
AND  
FRED IBBOTSON

*WITH ILLUSTRATIONS*

LONGMANS, GREEN, AND CO.

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TO THE  
PIONEER OF METALLOGRAPHY  
HENRY CLIFTON SORBY, LL.D., F.R.S., Etc.  
WHOSE RESEARCHES ARE AMONGST OUR  
EARLIEST SCIENTIFIC RECOLLECTIONS, THIS VOLUME IS  
RESPECTFULLY DEDICATED BY HIS  
FELLOW-CITIZENS, THE  
AUTHORS



## PREFACE.

IN the following pages we have dealt with the Analysis of Steel Works Materials on such lines as could profitably be followed in a large and busy Works Laboratory. The processes given in the books we have seen either

- (1) are too long and laborious ;
- (2) require too delicate manipulation ;
- (3) are too scanty in their treatment of the newer materials of steelmaking ; or
- (4) are not sufficiently accurate.

We believe that the special standpoint from which the book has been written makes it no worse a text-book for technical schools and colleges.

No man, in a lifetime, could choose the best from the continually increasing number of ways of analysing Steel Works Materials, and prove his chosen methods at every point. This has been our ideal, though we have by no means accomplished it. We have, however, described no method that has not been personally verified and practised for a considerable time, except in one or two minor (and mentioned) cases dealing with estimations we have never had occasion to make : and which have been added for the sake of completeness merely. In many instances we have imposed the still severer test of having estimations made by persons who were inexperienced in the particular process. And, moreover, in writing up the description we have simultaneously worked through the operation, so that no feature might be overlooked which was needful to a complete appreciation of the process ; most of the typical analyses given were obtained in this way.

The complexion of the entire book, as well as the particular methods described, undoubtedly somewhat reflect personal prejudices. But from the methods of which we had experimental knowledge we have always chosen the one made up of the simplest operations, and taking least time; it goes without saying of course that it must needs be accurate. There is certainly no ground for the supposition that the accuracy of a method is proportional to the elaboration of the apparatus and the number of operations it entails. On the contrary, of course, separations cannot be ignored, though they may be minimized by experience.

Generally the value of a process increases with the number of elements in whose presence the estimation can be accurately made. The investigation, from this standpoint, of every method regularly used in a laboratory is rather monotonous work, though less costly and hardly less time-consuming than the neglect of it. One knows a method well only by knowing its limitations. Those limitations once determined serve the double purpose of minimizing the danger of error and of eliminating a number of separations which, not uncommonly, introduce greater errors than they obviate.

In an introduction to the estimation of each element in Part I. we have discussed or at least mentioned the leading methods which have at any time been practised. This it seemed well to do, not only to show that there are many ways of doing the same thing, but also to suggest that one should actually know more than one way. In methods arranged on various principles, the behaviour of elements besides the one being estimated will also vary; and if the usual operations are interfered with by an unusual element a process may frequently be chosen which is not thus interfered with. This is a worthy consideration where large numbers of elements are being experimented with. It was not intended to add the Bibliography as an Appendix when these Preliminary Summaries were written.

One hears complaints that "the knotty points met with in one's business are most skilfully avoided in treatises and text-books." We should esteem it a favour to have any such omission on our part pointed out; moreover, we should be pleased to learn, from those

having very special knowledge, how any Section might be made more useful to those for whom the book is intended.

Most of the illustrations accompanying Part XI. were prepared from specimens belonging to the Metallurgical Department of the Sheffield University College, and we desire to express our gratitude to Prof. J. O. Arnold for permission to make use of these specimens and of many of his published micrographs. The section on Pyrometry was specially written for this work by Mr. A. M'William, A.R.S.M., to whom also our warmest thanks are due.

In speaking of work done, mention has occasionally been made of the doers of it, but in connecting names and processes, we have no intention of suggesting respective merit or priority.

H. B.

F. I.

BOWER ROAD, SHEFFIELD.





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## PART I. THE ANALYSIS OF STEEL.

### CARBON.

#### PRELIMINARY SUMMARY.

CARBON is estimated in steel more frequently than any other element. Although its amount is often many times less than that of the other constituents with which the preponderating iron is associated, carbon is generally regarded as the *sine quâ non* of the complex metallic substance called steel. Whether the manufacturer imagines it to impart the characters of steel to iron either by forming definite chemical compounds of iron and carbon, or by favouring the formation of allotropic modifications of soft iron, or whether, as is perhaps more usual, he entertains no definite opinion at all concerning its function, carbon undoubtedly occupies a pre-eminent position in his mind.

It has not always enjoyed this pride of place. For many years the claims of nitrogen as the steelifying element were ably supported, although such views are now generally discredited. That nitrogen has not, however, been entirely dispelled from the minds of metallurgists in this connection is evident from such occasional confessions as the following:—"I am inclined to think that nitrogen is a powerful agent in the conversion of iron into steel." (Roberts-Austen.)

According to Roberts-Austen (*Introduction to the Study of Metallurgy*), the fact that the difference between wrought iron and steel depends on the presence or absence of a small quantity of carbon was discovered by Bergman in 1781. This view of the matter failed to command immediate favour either with Bergman's contemporaries or with the workers of many subsequent generations; Bergman himself associated carbon with phlogiston, and made use of its extraordinary influence on the properties of iron to support a chemical theory already destined to demolition by the discovery of oxygen.

**Direct Combustion.** —The most obvious method of estimating carbon in steel is to burn the metal and collect the carbon dioxide. To accomplish this effectually necessitates a high temperature and a fine state of division of the metal. When one meets with the oft-repeated statement that such direct combustions yield low results, it is certain that one or both of these fundamental conditions have been violated.

Although the possibility of completely burning iron in a stream of oxygen is beyond doubt, the practicability of the process may be questioned. In order to assist the oxidation, the metallic borings have been mixed with various reagents including pumice, potassium chlorate, potassium chromate, lead chromate, hydrogen potassium sulphate, metallic lead, metallic copper, litharge, lead peroxide, red lead, bismuth trioxide, cupric oxide, phosphor-copper, zinc oxide, and alumina. With one or other of these reagents it is possible to make a direct combustion of the most refractory alloy obtainable.

Many attempts have been made to decompose the iron with acids, so that the liberated hydrocarbons might be burned to carbon dioxide, the volume of which could then be measured. When account had been taken of the residual carbon in the acid solution, these methods yielded low results owing to the formation of liquid hydrocarbons which escape estimation.

By adding chromic acid along with the sulphuric, the formation of liquid hydrocarbons and a carbonaceous residue is prevented, and the evolved gases, after drying, may be passed directly into the absorbing media. With some modifications this process is eminently practical and very convenient when a large number of samples which cannot be reliably submitted to the colour test has to be daily disposed of. The modifications relate to the complete conversion of the carbon into the dioxide. Using sulphuric and chromic acids only, some hydrocarbons are evolved and pass unabsorbed through the potash, if they have not been previously retained by the sulphuric acid used for dessication. These hydrocarbons, together with any trace of carbon monoxide may be burned to the dioxide by passing over heated copper oxide or platinized asbestos. It has been observed, however, that the hydrocarbons are generated principally at the beginning of the action, and that if copper sulphate<sup>1</sup> is added along with the mixture of acids,

<sup>1</sup> Ledebur (*Leitfaden für Eisenhütten-Laboratorien*, 5th ed., p. 67), who passes the evolved gases through a heated tube before absorption, says: "I have found by numerous comparative tests that the addition of copper sulphate is not only unnecessary, but really, particularly with graphitic irons, leads to the attainment of high results, probably in consequence of the formation of sulphurous acid."

the steel is protected by the deposited copper until a high temperature is reached, and thus the formation of hydrocarbons is minimized. Metallic mercury and phosphoric acid have also been used for the same purpose.

**Liberation of the Carbon.**—Those processes in which the carbon is liberated from the iron and then estimated are amongst the most accurate and reliable. By making a rod of the steel the anode of a dilute acid cell the iron dissolves, leaving the carbon *in situ*. This is the process of Binks and Weyl, and is more useful for specific research purposes than for daily use in a works' laboratory. The chief drawback, apart from considerations of time and convenience, is that some carbon escapes in the gaseous form. Blount corrects this error by placing the borings in a copper solution on a platinum plate, over which a copper plate is suspended, so that copper is removed from the borings on passing the current nearly as quickly as it is deposited on the copper plate.

The iron may be volatilized as chloride by passing over the borings a stream of chlorine gas. This process is often used for refractory alloys like ferro-chrome. The chlorine must be dry and free from oxygen, and is therefore sometimes passed over heated charcoal before reaching the steel.

The most extensively practised method of liberating the carbon is to dissolve out the iron by solutions of reducible metallic salts. Copper salts are generally used, and in order to avoid the precipitation of insoluble cuprous salts they are mixed in molecular proportions with the chlorides of potassium, sodium, and ammonium, or else strongly acidified with hydrochloric acid. Ammonium chloride is liable to contamination by pyridine hydrochloride, whilst large excesses of hydrochloric acid would cause escape of hydrocarbons. The former would yield a positive and the latter a negative error.

Acid solutions of the double copper salt give higher results than neutral solutions. This may be due to the slight solubility of the carbonaceous residue in such neutral solutions, or to the evolution of hydrocarbons: tungsten steels especially suffer loss of carbon in this way. (Foëster.)

The samples are usually dissolved in cold solutions, but Carnot states that in an atmosphere of carbon dioxide a temperature of 90° C. is permissible. With acidified cupro-potassium chloride there is a loss at temperatures exceeding 70° C.

The use of ferric chloride for dissolving the sample results in evolution of hydrocarbons; it may, however, be used for dissolving the precipitated

copper when the iron has been decomposed by the ordinary copper solutions.

The following methods of liberating the carbon have also been used :— decomposition of the sample in mercuric chloride (Boussingault), in fused silver salts (Berzelius), in iodine or iodine dissolved in ferric iodide (Eggertz), in a mixture of hydrochloric acid and bromine (Brand), in moist atmospheric air (Berthier), in a current of hydrochloric acid gas (Deville). Many of these processes are of historical interest only.

Much time may be lost in the liberation of the carbon. As long a period as ten days was found necessary to effect solution by some of the older methods. As a matter of fact, steel borings will dissolve in an acid solution of the double copper salts in from five to fifteen minutes, if shaken in a stoppered flask, and machines driven by small motors have been arranged to effect the shaking. An arrangement is described on page 13 for effecting the simultaneous decomposition of a number of samples when a few hours' delay is of no serious consequence.

**Estimation of the liberated Carbon.**—The liberated carbon may be estimated in a variety of ways. A simple but not precise method consists in drying the residue on a tared paper or in a Gooch crucible, the carbon contents being calculated from the loss of weight on ignition. Apart from the obvious interference of elements such as tungsten and chromium, which remain wholly with the carbonaceous residue, the percentage of carbon in the residue varies from 65 to 71 per cent., according to the nature of the sample. In some earlier processes the total loss on ignition seems to have been calculated as actual carbon. The residue is, however, really hydrated, and approximates in composition to the formula  $C_{12}H_6O_3$ . It can be easily nitrated, producing the coloured compound upon the formation of which the estimation of carbon by the Eggertz colour test depends.

*The dry combustion of the residue* is regarded as the most accurate means of estimating the liberated carbon. The drying of the residue calls for a little notice. Baker has shown that carbon containing moist oxygen gives rise to carbon dioxide when dried at  $100^{\circ}C$ ., and Carnot, we believe, burns the residue whilst still moist, so as to avoid any error through this cause.

The residue is sometimes mixed with copper oxide or lead chromate before igniting, but it is more convenient and quite as accurate to burn it alone. In order to avoid loss during the transfer from filter to ignition tube, various kinds of filtering tubes and wide-stemmed funnels, down which the residue could be bodily pushed, have been suggested. For the same reason the filtration and ignition can be made in the same

tube, and where only occasional combustions have to be performed there may be some advantage in such a procedure.

Where a regular series of combustions has to be made, we believe that a porcelain combustion tube is superior to one made of any other material. Some chemists prefer glass, and iron tubes closed with brass caps and leaden washers have been recommended. With suitable packing and appendages for retaining moisture, sulphur dioxide, hydrochloric acid, etc., any one piece of apparatus will give as good results as any other. The choice of tube, like that of the furnace itself, is chiefly a question of convenience and expense.

In all combustion methods the carbon may be calculated by measuring the carbon dioxide, or by absorbing and weighing it. Potassium hydrate solution, potash-pumice, and soda lime are the chief absorbents, but baryta, with weighing of the precipitated carbonate or its equivalent amount of sulphate, or titration of the excess of baryta, has also been used with success.

Phillips used potassium hydrate dissolved in glycerine. The potassium hydrate should be free from nitrite, the presence of which would lead to absorption of oxygen.

*The wet combustion* of the carbonaceous residue possesses some advantage over the dry combustion, as, apart from the matter of time occupied in drying, a much simpler form of apparatus will give very approximate results. Moreover, the measurement of the carbon dioxide in wet combustion entails no error due to imperfect oxidation, because any monoxide formed occupies the same volume as though it were dioxide. When, however, account is taken of small amounts of hydrocarbons and carbon monoxide by passing the gases over the heated copper oxide before absorbing the carbon dioxide, the process becomes more laborious than the *direct* wet combustion, which needs only the same precautions to yield accurate results.

**The Eggertz Colour Process.**—The hoary assertion that the intensity of the colour of a solution of steel in dilute nitric acid is proportional to the amount of carbon in the steel is never strictly true for any batch of steels.<sup>1</sup> The following facts relating to the colour of the solution show how inefficient artificial standards must be, and how very necessary it is to have a standard steel, whose history and composition are as nearly identical as possible with those of the sample.

<sup>1</sup> Ledebur (*Leitfaden für*, etc.) says:—"The test depends on the fact that the carbide carbon gives a colour to the nitric acid solution in proportion to its amount, and that the proportion of carbide carbon to the total carbon is the same for steels which have been cooled or heated in the ordinary manner."

1. The colour is darker the more rapidly the sample is dissolved.
2. The colour is bleached by daylight.
3. In hardened steel there exists a form of carbon which is decomposed by nitric acid without production of colour at all.
4. The colour is destroyed by continued heating, with evolution of carbon dioxide.
5. The colour is not entirely un-influenced by the amount of silicon, of phosphorus, of sulphur, and of chromium.

Stead's modification of the Eggertz test, in which an excess of caustic soda is used to precipitate the iron, and carry the colour into the filtrate, is more reliable under varying conditions than the original process. The colour of the filtrate is compared with suitable standards.

Other processes depending upon observations of colour or turbidity are:—Dupre's, in which the carbon dioxide from the burned carbon is passed into basic lead carbonate, and the cloud obtained compared with standard turbidities; Clerc's, in which the carbon dioxide is measured by the number of tubes of a solution of an alkaline manganate it can convert into permanganate; and Peiper's, where the streaks made by the samples on unglazed porcelain are treated with cuprammonium chloride, and compared with streaks made by standard bars.

**Graphite.**—When the sample is dissolved in hydrochloric or sulphuric acid, the residue must be washed with caustic alkali and alcohol or ether, in order to remove silica, and carbonaceous matter other than graphite. Mixed hydrofluoric and nitric acids have also been used to eliminate silica. When the silica is not removed, and the graphite is determined by loss on ignition, Tamm divides the weight of the residue after ignition by 0.94 to allow for water contained in the silica. The most accurate way, according to Shimer, is to dissolve in nitric acid, and thus to decompose carbide of titanium, which is not attacked either by hydrochloric or sulphuric acid.

## THE ESTIMATION OF CARBON.

### Direct Combustion: in the Dry Way.

Mysteriously high results are frequently the consequence of dirt, particularly greasy matter, when carbon is determined by combustion. Whenever possible, a dirty sample should be incontinently rejected. When no choice is offered (a rare contingency) visible impurities should be picked out, and oily matter then removed by ignition in a current of nitrogen, or by repeated digestion with alcohol or ether.



The practical difficulties of the direct combustion of metals in oxygen have been already indicated in the summary (page 2). In many cases, however, the sample is submitted in a powdered form, or must be reduced to such a condition for other purposes, and in such cases the question of temperature need only be considered. With such an arrangement of the furnace as is depicted in Fig. 1, there is no difficulty in obtaining so high a temperature that it is impossible, or nearly so, to distinguish the boat when looking into the heated tube.

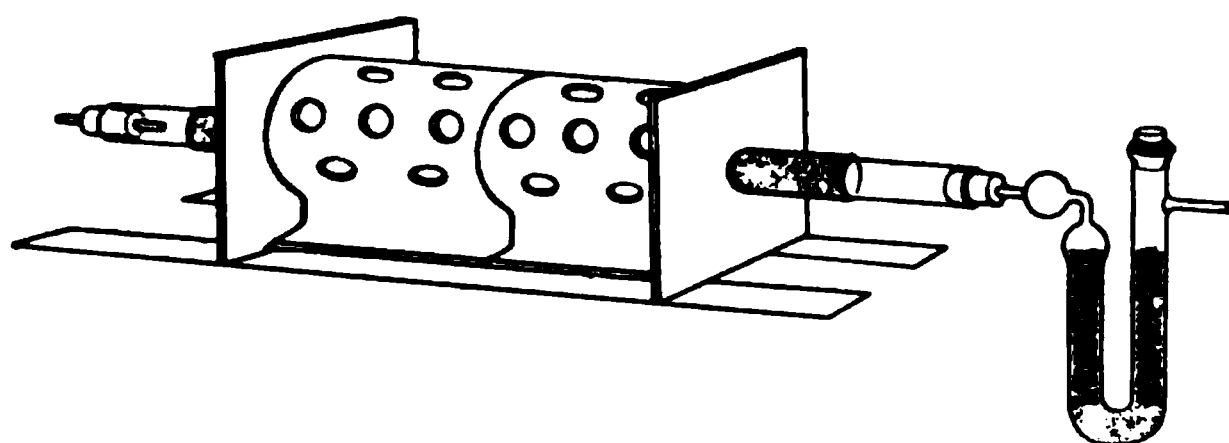


FIG. 1.



FIG. 2.

The porcelain tube is wrapped with asbestos millboard, one thirty-secondth of an inch thick, thoroughly soaked with water. This dries so firmly on the porcelain tube that no other fastening is required. Such a covering effectually prevents the cracking of the tube when the burners are lighted underneath. The asbestos arches are made from quarter-inch millboard, ten and a half inches long and four and a half inches broad. After suitably perforating and nicking slightly about an inch from each end, the well-wetted asbestos is pressed completely round a 2-inch bottle, and then squeezed on to the bench with the nicked edges spread out, so that after adjusting on the furnace the cover may have the shape shown in Fig. 2.

By their extreme lightness these covers are well adapted for temporary furnaces of frail build.<sup>1</sup> The ends and bottom of the cover are also closed by millboard suitably perforated to accommodate the combustion tube, gas-jets, and air supply respectively. A second and larger asbestos arch may be used over the first to concentrate the heat on any particular part of the tube. The incoming air or oxygen is purified in the usual way with caustic potash and calcium chloride, and the outgoing carbon dioxide, etc., by copper oxide and lead chromate or peroxide (in the tube), and calcium chloride and anhydrous copper sulphate pumice in the U tube (Fig. 1).

<sup>1</sup> Asbestos arches of this pattern were designed by one of the authors in 1897, and a description of them published in 1898 by his friend Jervis. (*C.N.* lxxvii. 5.)

The aspirator deserves a word. In order to keep the pressure of the oxygen inside the tube less than that of the atmosphere, and thereby facilitate the passage of air, some form of aspirator is necessary. A bottle merely with an opening at the bottom is objectionable, inasmuch

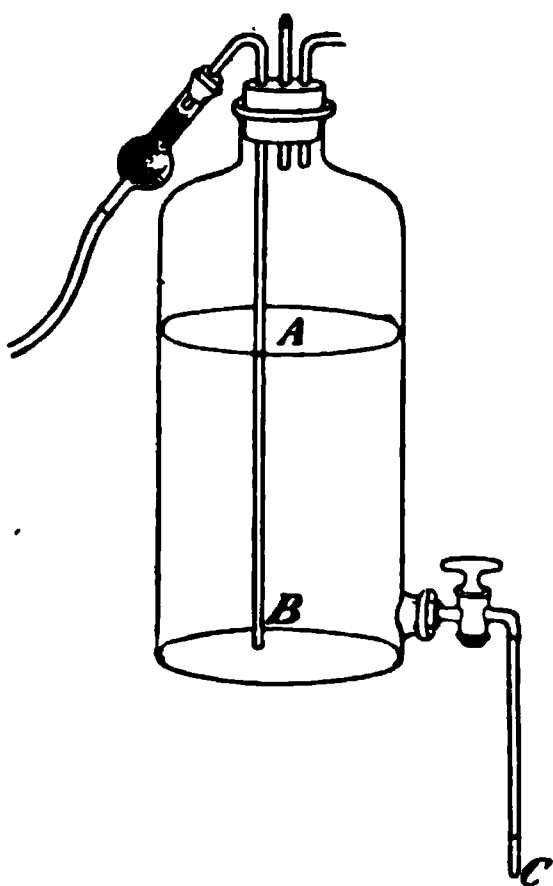


FIG. 3.

as the suction exerted is constantly decreasing as the bottle empties itself. The arrangement shown in Fig. 3 is not open to this objection; there is a constant pressure, determined by the column of water *BC*, independent of the water level inside the bottle. The distance *BC* can be increased or decreased by sliding the rubber tubing up or down the glass tube. With some means for carrying away waste water, and a fixed water supply to fill up the aspirator as required, this arrangement will be found to be eminently satisfactory. With such a furnace as the one just described, or with any other capable of reaching a bright red heat, the direct combustion in a current of oxygen can be made of the following

materials: metallic tungsten, ferro-tungsten containing not less than thirty per cent. of tungsten but free from chromium, ferro-silicon, silico-spiegel, metallic molybdenum, ferro-molybdenum, rich molybdenum-nickel, ferro-vanadium, and ferro-titanium.

Twenty per cent. spiegels give slightly low results; ferro-manganese gives very low results unless mixed with previously ignited zinc oxide, in which case the full carbon contents are yielded.

The materials just mentioned are completely decarbonized in a short time; it is stated that metallic chromium alloys can also be decarbonized by heating for about thirty hours. Such alloys can be completely burnt in as many minutes by mixing with a suitable oxidizing agent. Of the reagents already mentioned (page 2), copper oxide, lead chromate, and the oxides of lead have been most extensively used. Copper oxide requires a higher temperature than lead chromate, and lead chromate a higher temperature than litharge to effect complete oxidation in the same time. For the first two reagents there are many furnaces in use which do not yield a sufficiently high temperature; but none, we imagine, that are incapable of effecting decomposition when litharge is used. Litharge, however, is open to the objection that it takes up carbon dioxide from the air, thus neces-

sitating a blank determination; the amount of the blank, moreover, is by no means constant. Good samples of lead peroxide and red lead also yield a blank amounting to about 0.1 per cent. of the weight of the oxide used, but this amount is constant, so that these higher oxides are preferable to litharge. Bismuth trioxide may be prepared practically free from carbon compounds by fusing the basic nitrate; it does not absorb carbon dioxide from the air, and would merit constant use if the price were not prohibitive.

The powdered alloy, mixed with from three to five times its weight of red lead by shaking in a weighing bottle, is transferred to a porcelain boat. The boat is placed in the cool combustion tube and the temperature gradually raised to prevent too violent a decomposition. Some metallic lead is formed during the oxidation of the carbon, and oxygen is absorbed rapidly in the subsequent oxidation to litharge.<sup>1</sup> The supply of oxygen should therefore be increased at this stage. When strongly reducing alloys like ferro-silicon, spiegel, and ferro-manganese are combusted with these easily reducible oxides, the lead (or copper) formed runs into large beads. These beads are not only not readily re-oxidized, but they may occlude some undecomposed material, for which reason zinc oxide is to be preferred for such of the ferro-manganese alloys as cannot be burned alone in a current of oxygen. Zinc oxide is of no use for chromium and the more refractory alloys.

Where for any reason the mixture must be kept in the furnace for more than an hour a coating of thin wetted asbestos millboard on the outer surface of the boat absorbs such of the melted litharge as would creep over the edge and mess the inside of the tube. The covered boat must be ignited before using.

This form of the direct combustion in the dry way can be used also for every-day samples of steel, and is indeed a very suitable process for those works where the frequent occurrence of unusual elements and quite unknown steels cause the results of the colour test to have an uncertain value, and where at the same time the results are required quickly.

If the borings are coarse and heavy, throw them on to a sieve having twenty or thirty meshes to the lineal inch. From the sieved portion weigh out two and a half grams, mix by shaking in a small bottle with six grams of red lead, transfer to a boat, and at once burn in a current of oxygen or air. After the tube is thoroughly

<sup>1</sup> The absorption is sometimes so energetic that when glass tubes are used the hot soft glass is drawn so tightly round the boat as to render any further passage of oxygen impossible.

hot, twenty minutes' burning and the passage of two or three litres of air (or oxygen) through the tube is sufficient to decarbonize any kind of steel, *i.e.* if the furnace is a hot one, as we have previously urged it always should be for this kind of work. The carbon dioxide is absorbed as may be preferred in caustic potash or in soda lime, and, after deducting the blank due to the reagent, the increased weight calculated to percentage carbon. With high carbon steels there is a noticeable evolution of gas on heating the boat, but it is always comparatively slight, and is no reason why the boats should not be changed without cooling the tube.

The determination in this way is simpler than the mere combustion of the liberated carbon. The combustion tube need contain only a short heated column of copper oxide. Lead chromate or any similar body to retain sulphur compounds is unnecessary, and so also is copper sulphate pumice, or any other device for retaining chlorine compounds. In this respect the direct *dry* is simpler than the direct *wet* combustion to be described immediately.

Unless a boat is perfectly sound, free from surface cracks, etc., it should never be used; it may break in the tube, and besides being otherwise objectionable a coating of fused litharge increases the original tendency of the tube to crack with sudden changes of temperature. Immediately the boat is withdrawn from the hot tube the mixture is so soft that it may easily be cleaned out.

There is no danger that the sieved portion of the steel may contain more or less than its due portion of carbon.<sup>1</sup> The following series of results shows that the sieved and unsieved portions contain the same percentage. This remark applies to all kinds of special steels, but not, of course, to steels containing graphite or to pig-irons.

#### PERCENTAGE CARBON IN

Sieved portion.	Unsieved portion.
0·136	0·120
·447	·447
·758	·754
1·060	1·036
1·243	1·243
2·286	2·291

The combustion may be made on five grams of sievings with equally

<sup>1</sup> If a steel were very difficult to bore the abrasion or chipping of the drill might contaminate the sample in such a way as would be increased by sieving.

Two or three times during an extended use of this method the results have been as much as a tenth per cent. too high. At present no explanation can be given.

good results, but it is then desirable to pass the oxygen or air for about an hour and to increase the red lead to eight or ten grams.

This form of the direct combustion was worked out in 1898 in the laboratory of Messrs. Thomas Firth & Sons by one of the authors. A paper from the same laboratory by R. Leffler (*C.N.* lxxxiv.) gives other interesting particulars.

#### Direct Combustion : in the Wet Way.

The direct wet combustion can be used with advantage and satisfaction for making daily assays of large numbers of samples if a suitable form of apparatus is used. We saw such estimations made at Messrs. Charles Cammell & Co.'s Grimesthorpe Works, and we are indebted to members of the laboratory staff for the following account of the operation and the photograph that illustrates it, Fig. 4.

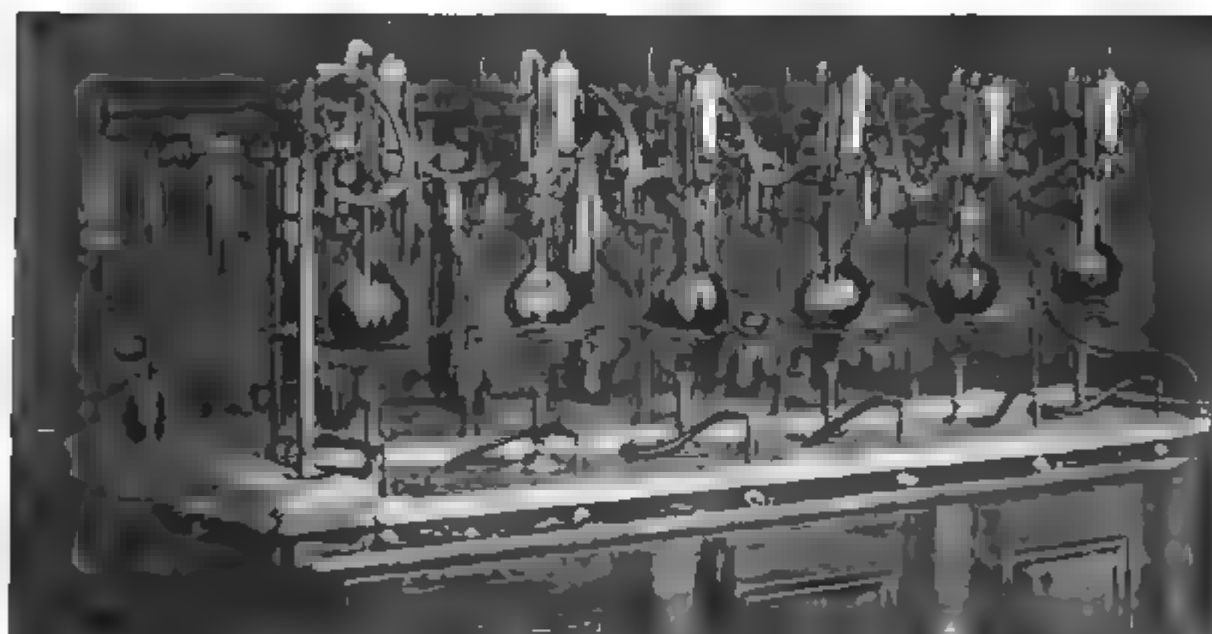


FIG. 4.

The details are more clearly visible in the drawing of a single piece of apparatus, Fig. 5. The Bunsen pump is connected under the bench with a large bottle which acts as a vacuum reservoir.

"The tube for absorbing the carbon dioxide contains, in the bulb, very small granules of freshly heated calcium chloride. The stem contains soda lime which has been slightly moistened and finely powdered. The effectiveness of the tube can be seen at any time because the absorbed carbon dioxide bleaches the soda lime and leaves a sharp line dividing the used from the unused material.

"The mixture of chromic acid and copper sulphate is made by

dissolving one pound of each in boiling water and making up to 2700 cubic centimetres.

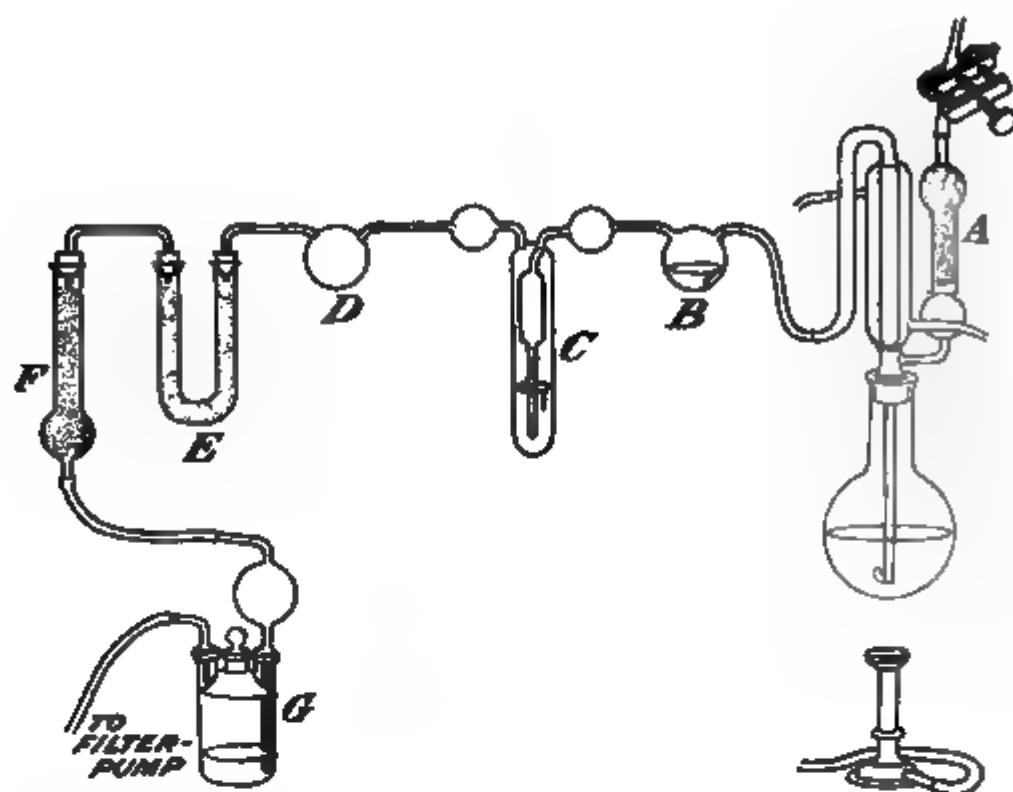


FIG. 5.

- " A contains calcium chloride in the bulb and powdered soda lime in the stem; it is fitted with a screw clip for regulating the air supply.
- B is an empty bulb.
- C contains strong sulphuric acid.
- D is an empty bulb whose object is to prevent any spray of acid getting to E.
- E contains dry calcium chloride.
- F is a soda lime tube for weighing the carbon dioxide.
- G is a sulphuric acid guard tube for the suction arrangement.

"For each estimation 170 c.c. of this mixture is placed in the flask along with 185 c.c. strong sulphuric acid. The flask is then placed in position on the wire gauge, the screw clip for regulating the air closed, and the pump set going; all joints in the apparatus being tight a flame is placed under the flask. When the liquid boils and has displaced the air the screw clip is loosened and a steady current of air allowed to pass for half an hour, then the light is turned out and the pump stopped.

"The steel drillings are put through a double sieve, a fine meshed one at the bottom and a coarse one above, so that only drillings of about one-twentieth of an inch cube remain between, the very fine and very coarse being rejected. By this means the steel always takes about the same time to dissolve i.e. about an hour. The amount weighed off is 5.4544 grams, so that the weighed carbon dioxide only requires dividing by two to give the percentage carbon.

“When the acid has cooled for about fifteen minutes, the flask is removed, the weighed soda lime tube attached, the drillings added and the flask quickly replaced. The liquid is then started boiling in the same order of procedure as before, the air being allowed to pass a little while after the steel is dissolved before detaching the absorption tube for re-weighing.”

We asked the gentleman who designed the particular form of flask shown in the illustrations, whether he thought the use of copper sulphate was necessary, and drew his attention to Ledebur's statement (footnote, p. 2). He said, “A series of experiments made in comparison with the dry combustion method of the separated carbon convinced me that the results were not too high. The results were :

	I.	II.	III.	IV.	V.	VI.
Direct wet combustion, - - -	·734	·545	·205	·253	·286	·593
	·742	·545	·210	·251	·291	·586
Dry combustion of liberated carbon, -	·706	·539	·221	·258	·294	·597
	·735	·532	·224	·247	·291	·570

By omitting the copper sulphate altogether the results were lower, but at the same time they were erratic.”

#### Liberation of the Carbon and Dry Combustion.

This method is described as it may be worked for the estimation of carbon in about a dozen samples per day, the results being returned the day after receipt of the samples. Place the weighed drillings (5 grams) along with a saturated solution of cuprammonium (sodium or potassium) chloride containing 5 per cent. of free hydrochloric acid, in a pattern flask. Attach one flask to another as shown in Fig. 6. The first flask is joined to a Woulff bottle containing some mercury, below the surface of which the long narrow tube just dips so as to prevent any movement of liquid from one flask to another, in case the flow of water should either cease or come too quickly. The last flask is joined to a similar bottle containing lead acetate solution through which the air is aspirated. The flasks depicted in the figure were designed by James Taylor in 1884. They possess the advantages of being easily washed during filtration, and of having so small a base that the borings must always lie near the incoming air current. The number of separate samples which may be dissolved at the same time is determined by the amount of pressure produced by the flow of water, and this should be sufficient to agitate more than the accustomed number, so that each day's batch may be all dissolved

during the night. On the following morning complete decomposition should have been effected, even when stout wire or small screws, from which borings cannot be easily got, have been placed in the flasks. After loosening the stopper, wash the longer tube first with hydrochloric acid and then water, to remove any basic ferric salt and to detach carbonaceous particles.

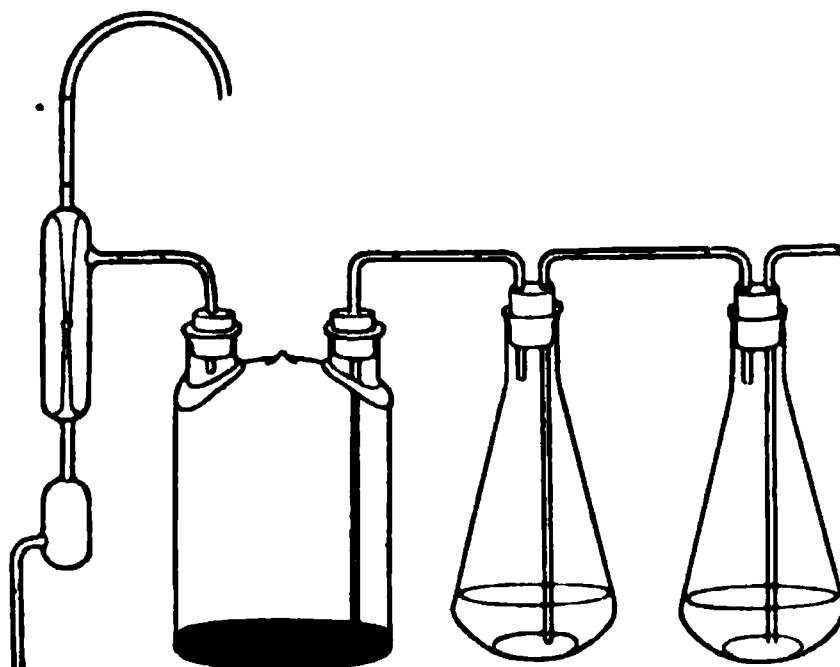


FIG. 6.

A filter made from picked half-inch asbestos fibres which, after digesting with hydrochloric acid and washing, have been ignited and shaken with water allows the solution, but not a trace of the residue, to pass through at so quick a rate, particularly if the filter is prepared by means of hot water, that two or three samples occupy one operator's time. The mode of transfer from filter to boat is worthy of consideration. Arrange the numbered or lettered boats on a clean porcelain slab, and have at hand some dry asbestos and distilled water in cover glasses. Suck away the superfluous water from the filter by means of a small aspirator bottle, hold the funnel in the left hand, and with the point of a slim pair of forceps turn up the edge of the asbestos filter, fold it on itself and place it open edge downwards in the boat, and remove the perforated porcelain filter plate. Press a tuft of moistened asbestos held in the forceps against the throat of the funnel, and as the funnel is revolved by the left hand, gently draw the asbestos towards the rim. Hardly a trace of carbon can be seen after this, but in order to make certain of having collected it all, it is advisable to repeat the last operation, examining the rim of the funnel very carefully for any adherent particles. In about an hour or an hour and a half the twelve samples should have been filtered and transferred to the drying oven. The drying occupies from one to two hours.

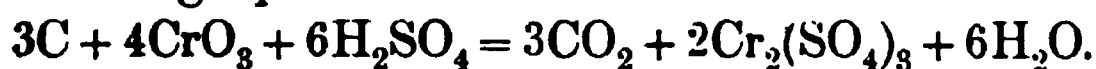


The combustion tube at a red heat must of course be air tight. It is safest to test this by attaching the Geissler's potash bulbs and alternately stopping and starting the air current. The boat is pushed into the red hot tube, the stopper quickly replaced, and the aspirator joined up. One and a half to three litres of air are aspirated at a quick rate according to the amount of carbon dioxide to be carried forward and the amount of air to be displaced before the carbon dioxide reaches the potash bulbs. The only piece of apparatus we use between the combustion tube and the potash bulbs is a U tube containing calcium chloride<sup>1</sup> in each leg, and anhydrous copper sulphate in the bend, and we find that a litre and a half of air completely carries three decigrams of carbon dioxide into the potash. After twenty to thirty minutes' burning the combustion is completed; the boat may then be removed and another one introduced at once. With fresh potash and a well-packed calcium chloride prolong, the combustion can be made actually in half the time mentioned without any danger of loss.

The state of desiccation of the gases as they pass into and out of the potash bulb should be the same. A blank estimation, omitting the carbon, should, however, occasionally be made, and any increase or decrease in the weight of the bulb allowed for in the actual estimation. This source of error is sure to arise in an erratic manner if calcium chloride is used, as bought, without further and uniform drying.

### Volumetric Estimation of the Liberated Carbon.

For this operation the samples must be completely dissolved: on washing the residue with hot dilute sulphuric acid the filtrate should not decolourize a weak solution of permanganate. The principle of the process is that of the ordinary wet combustion of the liberated carbon with chromic and sulphuric acids, the only difference being that standard solutions of chromic acid are used and the excess determined, instead of measuring the carbon dioxide evolved. The oxidation is readily carried out in small beakers arranged in a constant level water bath, as shown in Fig. 7. Powdered potassium bichromate is dissolved in sulphuric acid diluted with its own volume of water. A four decinormal solution is a convenient strength, and as the reaction takes place according to the following equation:



<sup>1</sup>Calcium chloride tubes, before using, should be subjected to a current of carbon dioxide and then a large volume of air. This treatment carbonates any lime present in the calcium chloride.

25 c.c. of the  $\frac{4N}{10}$  bichromate oxidizes one per cent. of carbon when operating on three gram samples. It is well known to be practicable with decinormal bichromate solutions to titrate to one-tenth of a c.c., which under the above conditions is equivalent to about 0.001 per cent.

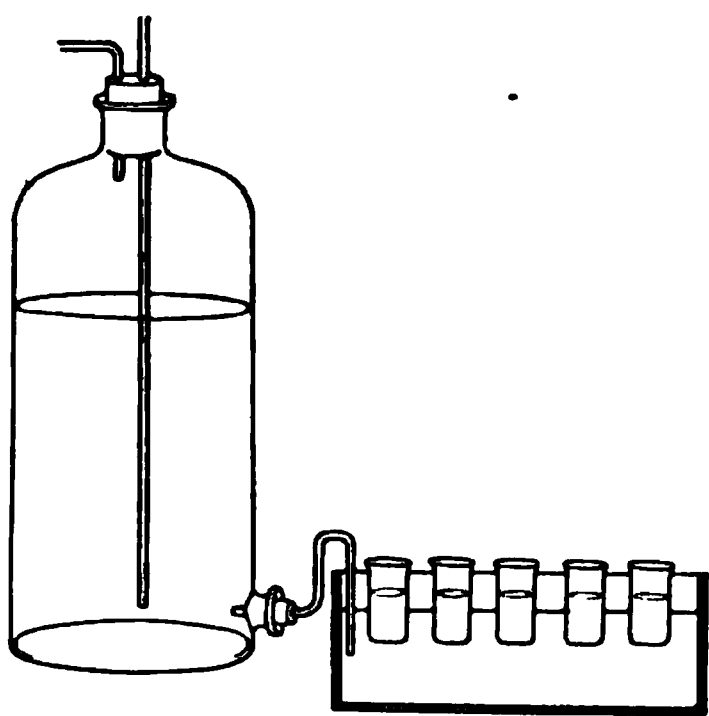


FIG. 7.

carbon, so that the errors of manipulation are of that insignificant kind so desirable in technical analyses.

During the oxidation of the carbon the asbestos entangles liberated carbon dioxide, and is floated to the surface of the liquid. This necessitates occasional stirring, but at the same time it gives longer contact with the oxidant, and thereby promotes the complete oxidation of any carbon monoxide that might be generated. When the asbestos lies

quietly in the solution, and a gentle stirring causes no appearance of bubbles, the reaction is at an end. The solution may then be diluted and titrated with ferrous sulphate solution and the bichromate used for the oxidation. Each c.c. of bichromate reduced during the oxidation of the carbon represents 0.0012 gram of carbon.

The rate of oxidation depends on the temperature and the amount of stirring. In a calcium chloride bath at 130°C., and with constant stirring, the carbon from three grams of a 1.25 per cent. carbon steel may be oxidized in ten minutes. In a water bath at 100°C. the time occupied is twice as much, whilst with such occasional stirring as could be given to a batch of eight or ten samples in a water bath at once, an hour's digestion is ample.

Larger amounts of carbon, requiring more of the standard bichromate solution than can be accommodated in the small beakers, may have powdered bichromate, free from organic matter, added along with 30 to 50 c.c. of the acid solution.

Any class of material which is decomposed by the double copper salt without leaving reducing matter in the residue may be successfully assayed for carbon by this process. The metallic tungsten from tungsten steels reduces bichromate solutions at an appreciable rate only when the sulphuric acid is dilute, so that if the digestion with the half and half sulphuric acid solution of the bichromate is not unduly prolonged, and the titration after dilution completed rapidly, the results are only a few

hundredths per cent. too large. The oxidation of the metallic tungsten is very much lessened by using concentrated sulphuric acid along with powdered bichromate, but in such a solution the carbon is oxidized much less speedily. The process is not applicable to chromium steels, because this metal is left in the carbonaceous residue as a double carbide.

The graphitic carbon of pig irons is much less readily oxidized than combined carbon, using the half and half sulphuric acid solution. Ninety parts of sulphuric acid, with ten parts of water, is the best strength of solution to use for graphite, but curiously enough the combined carbon is as badly oxidized by the stronger acid solution as graphite by the weaker. This fact should considerably modify the practice of using as strongly acid solution as possible in the ordinary wet combustion of the residue, and we consider the experimental results upon which it is established of sufficient interest to merit publication.

Amounts of combined carbon and of graphite, liberated from steel and pig iron respectively, and equivalent in each case to 1.18 per cent. when calculated on three grams of the metal, were digested with 0.7 grams of powdered bichromate and 30 c.c. sulphuric acid solution of the strengths specified in the following table. The digestions were made at 100° C. in batches of four, the samples being stirred continuously in succession :

Parts Concentrated Sulphuric Acid in 100.	Percentage Oxidized of		
	Combined Carbon.		Graphite.
	Digested 30 mins.	Digested 15 mins.	Digested 30 mins.
10	0.58	—	0.04
20	0.77	—	0.09
30	0.90	—	0.12
40	1.05	—	0.17
50	1.17	1.04	0.31
60	1.19	1.12	0.47
70	1.20	1.08	0.62
80	1.10	0.81	0.78
90	0.59	—	1.07
100	0.35	—	1.00

The volume of sulphuric acid used has very little influence on the speed of the oxidation, so long as there is sufficient bulk of liquid to permit free movement of the carbonaceous residue and the filtering medium on which it was collected.

Of importance also in this connection is the following table, showing the spontaneous reduction of chromic acid by sulphuric acid when kept at varying temperatures for three hours. The figures show the percentage of chromic acid undecomposed at the end of the operation :

Parts Concentrated $\text{H}_2\text{SO}_4$ in 100.	Temperature of Digestion.				100° for 16 hours.
	130°	120°	110°	100°	
30	100·0	—	—	—	—
40	100·1	—	—	—	—
50	100·1	—	—	—	99·9
60	98·6	99·2	99·6	99·9	99·0
70	91·3	98·2	99·0	99·6	97·6
80	88·7	95·1	96·5	98·1	88·7
90	91·3	95·8	96·8	98·2	92·6
100	94·8	—	—	—	97·6

At 130° C., in a bath of calcium chloride, the residue from 1·5 grams of a highly graphitic iron was completely oxidized by the weaker acid solution in an hour and a half; the same time was occupied in the strong acid at 100° C., whilst at 130° C. the time required was less. Both of these latter procedures introduce a positive error due to the action already mentioned, and exemplified by the table given above. This error is as a rule less than that due to imperfect sampling when the drillings are weighed from a packet in the ordinary way.

#### The Estimation of Carbon by the Eggertz Colour Test.

A description of the *modus operandi* of this test is not contemplated here. It can be met with in any text book on quantitative analysis, and the method is familiar to all chemists acquainted at all with steel analysis.

The value of the process as a means of gauging the percentage of carbon is beyond question, so also is its value as a method for the estimation of the carbon when steel is being produced under well-defined and invariable conditions. To rely on its indications, however, with samples of unknown origin is to ignore the limitations of the method, to invite confusion, and to discount the value of analysis in the mind of the steel maker. These limitations, as determined by various observers, and concerning which there is a general concensus of opinion, are set forth on page 6. When the estimation of carbon by combustion was a long and tedious affair, some such means of

correcting results (according to the indications of the condition of the carbon afforded by the dissolving sample) as those practised by Parker (*Chem. News*, xlii. 88) were perhaps justifiable when used by skilled persons, but with so many aids now to hand of making rapid combustions, any modification of the colour (or any other) method, in which one's desires might warp one's judgment, should be studiously avoided.

The colour test is useful at the furnace for making rapid tests of bath samples, and for controlling the output of material which does not vary, or varies only in well-known ways, but it is an accurate method of estimating carbon only under ideal conditions. The one or two decigrams taken for the test are as nothing to the total weight of material they are intended to represent, and some chemists on this account favour the practice of dissolving a gram or two of sample and of standard, aliquot parts of the solutions being then compared. There may be some advantage in this when the test is used for such heterogenous material as cemented bar, but obviously from the difficulty of obtaining either a fair sample or a suitable standard, the assay of such material for carbon by the colour test is fraught with uncertainty.

The brown flocks, which are last to pass into solution and to which the colour is due, are, according to Donath, identical with the product obtained on nitrating the carbonaceous residue left on treating steel with a solution of a double copper salt. They have the composition  $C_{47}H_{32}(NO_2)_2O_{25}$ ; other authorities, however, give slightly different figures. The oxidation of this interesting compound can be observed by adding standard permanganate solution to separate solutions of the same steel in dilute nitric acid, from the time the sample is dissolved until all the flocks have passed into solution or further, then boiling and titrating the excess of permanganate with ferrous sulphate. In this way, with steels of the same kind, results can be obtained roughly proportional to the amount of carbon, but the operation is fraught with all the disadvantages of the ordinary colour test, and is scarcely worthy of mention as a means of estimating carbon in steel.

Stead's modification of the Eggertz test, the results of which, according to its author's experiments (*Journal of the Iron and Steel Institute*, 1883, 213, and *Chem. News*, xlvii. 285) are not influenced by moderate excesses of heating, of nitric acid, or of sodium hydrate, is particularly serviceable for low carbon steels, as the colour of the carbonaceous matter in the alkaline filtrate is more than twice as intense as that

which it imparts to the acid solution. Moreover, some of the metals which impart a colour of their own to the nitric acid solution (chromium, nickel, copper) are precipitated by the soda along with the iron. Traces of chromium sometimes pass into solution as chromate when solutions of a chromium salt are precipitated with strong alkalis.

### **The Estimation of Graphite.**

Carbon is occasionally transformed from the combined to the graphitic state during the mechanical preparation of hard steels such as file steel or drill steel, but graphite has most frequently to be estimated in pig irons.

The most exact and least troublesome process is to dissolve the sample in nitric acid, s.g. 1.20, digest until all the floccs due to combined carbon have passed into solution, filter, and burn the residue. Both hydrochloric and sulphuric acids have been used for effecting decomposition, but apart from the fact that any titanium carbide present is left undecomposed, neither of these acids effect the complete evolution of the combined carbon as hydrocarbons, and complicated washings have to be resorted to. In this connection, a few remarks on the process of sampling, which adds not a little to the uncertainty of graphite determinations, may conveniently find a place.

The importance of procuring a sample thoroughly representative of the material under assay cannot be overrated. Some materials are particularly liable to yield unfair samples; converted bar irons, for example, which decrease in carbon towards the centre. These are most accurately sampled for the chief element by taking a small hole right through the bar and using all the drillings. Steel-faced articles, such as wortles or draw plates, may be examined satisfactorily only by taking a broad thin cut from the steel and iron faces respectively, and also drilling a hole right through the thickness; the data obtained from the three samples enable one to calculate the depth of the steel facing. Pig irons should not be drilled at the centre of a fractured surface, but from the curved to the flat side. Shimer recommends the moistening of the borings with alcohol, so as to make the powdery graphite to cohere uniformly with the borings. A sample is then removed and dried. Good results may be obtained by sieving out the powder, and weighing out proportional amounts of the fine and coarse particles on the same principle as that of allowing for "metallics" in dry assaying. Errors of three or four tenths per cent. in the estimation of graphite can easily be made

when the sample is weighed from a packet of drillings in the ordinary way; these errors are thrown on the combined carbon when that constituent is determined by difference. As an extreme case, it is even possible to get a graphitic percentage greater than the sum of the actual graphitic and combined carbon percentages.

### Other Varieties of Carbon.

Ledebur distinguishes four different modifications of carbon, viz.:—graphite, temper carbon, carbide carbon, and hardening carbon. The following means of distinguishing or estimating these varieties are taken from Ledebur's *Leitfaden für Eisenhütten-Laboratorien* and his paper in the *Journal of the Iron and Steel Institute* for 1893. See also Juptner's paper, *J.I.S.I.* 1897, i. 248.

*Graphite and Temper Carbon.*—When iron is dissolved in acids the temper carbon behaves exactly like graphite, and at present there are no means of separately determining the two modifications when they occur together. Temper carbon differs from graphite by its amorphous condition, and still more in that when the iron is heated under oxidizing conditions—with iron ore, for instance—it somewhat rapidly disappears, whilst graphite remains unaffected under similar treatment. Temper carbon is formed only by long heating of high carbon steels or white irons.

*Carbide Carbon* is that carbon diffused throughout the iron as  $\text{Fe}_3\text{C}$ . Abel isolated it in the first instance by decomposing the steel with a mixture of bichromate and sulphuric acid; it is estimated by Ledebur (and also by Müller) as follows:—Treat from one to three grams of the finely divided material with from 30 to 90 c.c. very dilute (1 to 10) sulphuric acid until the residue yields to the pressure of a glass rod. The operation is performed in the cold, air being excluded by a stream of hydrogen or coal gas; the time taken may vary from two to six days. When completely decomposed filter on to asbestos, and burn the residue to carbon dioxide in the usual way. The result represents the carbide carbon and the graphitic and temper carbon, the latter being otherwise determined and deducted.

*Hardening Carbon* causes the evil-smelling hydrocarbon gas which is given off when steel is treated in the cold with hydrochloric or sulphuric acid. Possibly it could be determined by passing the gas in a stream of hydrogen over heated copper oxide, but the simpler way is to deduct the other three forms of carbon from the total carbon, and thus obtain the hardening carbon by difference.

The following table shows in what amounts the various carbon compounds occur in some common materials :

Material.	Graphitic and Temper Carbon.	Carbide Carbon.	Hardening Carbon.	Total Carbon.
Deep Grey Pig, - - - - -	3·33	0·44	0·00	3·77
Light do., - - - - -	2·40	·73	·17	3·30
White Pig Iron, - - - - -	·16	1·88	·54	2·58
Spiegel (11% Mn), - - - - -	·00	3·09	1·41	4·50
Chilled Castings, - - - - -	·19	2·43	·58	3·20
Tool steel : normal cooling, - - - - -	·00	·81	·22	1·03
Do. hardened in water, - - - - -	·00	·38	·65	1·03
Do. hardened and blue tempered, - - - - -	·00	·67	·36	1·03
Basic Bessemer, - - - - -	·00	·17	·05	·22
Do. hardened in water, - - - - -	·00	·17	·04	·21

SILICON.

PRELIMINARY SUMMARY.

The methods for the estimation of silicon in steel depend mainly on the use of various acids and mixtures of acids. The following are or have been in use: hydrochloric, hydrochloric and bromine, hydrochloric and sulphuric, sulphuric, sulphuric and aqua regia, and aqua regia alone. The decomposition of the metal with hydrochloric acid is associated with the earliest methods of estimating silicon. It fell into disuse for a time on account of the suggested escape of silicuretted hydrogen during the dissolving ; this suggestion, it has been shown, has no foundation in fact.

On dissolving iron in acids the amount of silicon passing into solution is least when hydrochloric, and most when nitric, acid is used. With nitric acid of 1·135 specific gravity all the silicon passes into solution ; on the other hand, so little passes into solution when strong hydrochloric acid is used that the collection of the silica without a preliminary evaporation to dryness has been suggested. For steels and iron at any rate the practice appears to be unsound. A. H. Allen has pointed out that when iron is dissolved in hydrochloric or sulphuric acids the silicon is liberated as leucon and not as silica, and as leucon is soluble in water no invariable proportion of the silicon can remain undissolved.



The addition of ammonium chloride is said to quicken the evaporation of hydrochloric acid or aqua regia solutions, and to prevent the silica being contaminated with manganese. The complete expulsion of nitric acid, and the addition of potassium chloride to prevent the decomposition of ferric chloride have also been insisted on ; but experience has shown that these are details of little or no importance.

Those methods in which the dissolved sample is evaporated with sulphuric acid are often spoken of as Drown's, or modifications of it, although the use of mixed acids and evaporation to sulphuric anhydride fumes was described some years before Drown's paper appeared. The improvements effected are mainly in points of manipulation, with the main object of increasing the speed ; in that particular they have a much wider application. Langmuir passes a strap round the beaker, holds the free ends together for a handle, and by a suitable movement of the hand keeps the liquid in constant motion over a naked flame. Jones, by arranging one burner underneath the basin and another to impinge on the surface of the liquid, completes the evaporation in five minutes. It is claimed to be advantageous to use a mixture of aqua regia and sulphuric acid rather than nitro-sulphuric acid, in that the dehydration of the silica is more perfect, and there is no bumping or spattering of the boiling solution.

Some discrepancies noticed in the analysis of the same material have been explained by the observation that when the acid solution is allowed to stand, after the dehydration, a portion of the silica is redissolved. But this explanation is not unanimously accepted ; there certainly are modes of working the nitro-sulphuric process which are subject to no such error.

The methods not covered by the above classification are : (1) Roasting the finely divided sample in the muffle so as to oxidize silicon to silica followed by digestion with hydrochloric acid to separate iron, etc. (2) Fusion with acid potassium sulphate followed by the same treatment ; and (3) Volatilisation of the iron and silicon together in a stream of chlorine, the silicon chloride being collected in water and separated in the usual way. By this last process any slag or cinder present remains with the carbon in the boat. If the slag is ferriferous, however, it may be partially decomposed by the chlorine ; in such cases the sample should be attacked with cuprosodic chloride or with bromine or iodine, and the amorphous silica accompanying the slag separated by digestion with aqueous sodium carbonate.

## THE ESTIMATION OF SILICON.

**By Evaporation with Nitro-sulphuric Acid.**

Dissolve 5 grams of the metal in as much as is needed of the following mixture :

Nitric acid, -	-	-	-	-	-	208 c.c.
Sulphuric acid, -	-	-	-	-	-	125 c.c.
Water, -	-	-	-	-	-	500 c.c.

Set the beaker at once in the centre of a very hot plate,<sup>1</sup> and allow to boil briskly to dryness with the cover on. Towards the end there is considerable frothing, and then, almost simultaneously throughout, the mass becomes lemon-coloured and fumes of sulphuric anhydride begin to rise. At once add warm water from the jet of the wash bottle: it must be as hot as possible without causing too violent a reaction with the sulphuric acid, and it should be added at this stage so as to prevent the cracking of the beaker as the dried mass cools. The assay may be allowed to stand two or three days after the water is added without fear of silica being redissolved, but it is obviously quicker to make use of the already heated solution by at once adding hydrochloric acid, boiling until only silica is undissolved, filtering, washing, and igniting as usual. The operation from end to end takes about an hour.

**By Evaporation with Hydrochloric Acid.**

Where only one fume cupboard is available for all classes of work including gravimetric estimation of sulphur after oxidizing with aqua regia, it is well to minimize the evolution of sulphuric fumes by using the hydrochloric acid process. The following is the mode of making the estimation as used at the Newburn Steel Works.

Dissolve 5 grams of the steel in 35 c.c. strong hydrochloric acid. When dissolved examine the solution for sand or slag; the first occurs in pig iron as a result of careless drilling, the second through small cavities getting filled with slag. Evaporate the hydrochloric acid as quickly as convenient until the mass solidifies, then remove to a cooler part of the plate, and continue heating until the yellow colour has all disappeared, *i.e.* until the mass is a dirty pink but not a deep reddish brown. When cool moisten with hydrochloric acid, add hot water, raise to boiling, and filter at once. Wash with cold

<sup>1</sup> Plates should be kept clean and regularly black-leaded.

acidulated water and weigh after ignition as usual. Mr. Hogg informs us that this process gives somewhat higher results than the nitro-sulphuric process, especially when the silicon is very low.

The only bodies existing in commercial steel or iron which can interfere with any of the acid processes are, tungsten, chromium, titanium, vanadium, and phosphides of iron. These all may be removed by fusion with acid potassium sulphate. The whiteness of an ignited precipitate is not positive proof of its purity: with hydrochloric acid evaporations it may contain titanic oxide, with sulphuric evaporations it may contain phosphides of iron.

When crude silica is evaporated with hydrofluoric acid it is important to remember that if the associated impurity is alumina, titanic oxide or lime, sulphuric acid *must* also be added, in order to prevent the formation of volatile fluorides of alumina and titanic oxide, or an undecomposable fluoride of calcium. The added sulphuric acid retains these oxides as sulphates until all the hydrofluoric acid is driven off; it is then equally important to remember that sulphuric acid can be driven off completely only at very high temperatures, *i.e.* over a good blast lamp and preferably assisted by the addition of ammonium carbonate.

## MANGANESE.

### PRELIMINARY SUMMARY.

A very large number of methods, based on many different principles, has been proposed for the estimation of manganese in steel either with or without a previous separation of the iron. Almost as great a diversity of opinion has existed also concerning their merits. There is of course no such thing as a *best* method even in the case of such a comparatively invariable material as steel; differences of opinion often obtain because "the advocate of one method makes another method suffer by comparison, more by reason of his own want of skill in its manipulation, than by reason of any great advantage possessed by his own."

**Separation of Iron from Manganese.**—The acetate separation of iron and manganese is probably the oldest, the most frequently practised, and the most misunderstood of any of the methods in which the iron is the element precipitated. This misunderstanding

amounting to confusion, is accentuated when nickel and cobalt, instead of manganese, are to be separated from iron; on this account a description of the principles involved will be found in connection with the estimation of these allied elements (see page 67). It will suffice to remark here that a re-precipitation of the iron, very often recommended, in order to separate small quantities of manganese supposed to have been precipitated along with the basic ferric acetate, is merely a waste of time and material, unless such excesses of acetate have been used as would precipitate many times the amount of iron actually present. Succinates and formates may be used instead of acetates; the former are said to completely precipitate aluminium as well as iron, and the latter to give a precipitate more easily washed than that produced by acetates. The neutralized solution of the iron and manganese may also be precipitated with other salts of the alkali metals, which offer possible advantages according to the process to be used subsequently for the estimation of the manganese in the filtrate. The chief of these are sulphates, which leave the aluminium partly in solution, and phosphates, which provide a filtrate very serviceable for the estimation of manganese as pyrophosphate. Chromates, tungstates, molybdates, and the salts of several organic acids may also be used in this separation, but there is no evidence to prove that they offer any special advantage.

The iron may also be precipitated with just as much sodium bicarbonate as is necessary to coagulate the neutralized solution, or by merely boiling the solution, after it has been so carefully neutralized that on standing in the cold it loses its transparency and tends to become more turbid. Both these processes need very skilful handling, both are assisted by the presence of ammonium chloride, and both are interfered with by the presence of aluminium. The coagulation of the neutralized solution with an emulsion of zinc oxide, in connection with the permanganate titration of the manganese (Volhard's process), is well known; the oxides of lead and mercury and the carbonates of lead and barium have been used in a similar capacity. With the exception of the use of sulphuretted hydrogen to precipitate nickel, cobalt, copper, etc., along with the iron from the acetate solution, all the other processes for precipitating the iron are with more or less reason little known and practised less. They include: precipitation with caustic alkali in the presence of much ammonium chloride, volatilization of the iron in a current of chlorine, precipitation, from ferrous solutions, of the iron, aluminium and chromium with sodium nitrite, and precipitation from acetic solutions with nitroso- $\beta$ -naphthol.

The chlorate process is best known of those which separate iron and manganese by precipitating the latter. The precipitate is never quite free from iron, and, therefore, the gravimetric is less popular than the volumetric estimation of the precipitated dioxide. The process is known in England and America as the Williams or Ford and Williams process; in Germany it is credited to Hampe or to Beilstein and Jawain. These latter chemists have suggested a method in which the solution of the metals is poured into concentrated potassium cyanide solution, and the manganese precipitated with iodine or hydrogen peroxide. In Classen's process an excess of neutral potassium oxalate is added, and the potassium manganous oxalate decomposed with acetic acid, the iron remaining dissolved. Manganese has also been precipitated from alkaline tartrate solutions by potassium ferricyanide. We have not known of any of these latter processes being regularly practised in a works' laboratory.

**The Estimation of the Manganese.**—The removal of the iron as basic acetate is nearly always associated with the precipitation of the manganese from the filtrate by means of bromine, with final weighing as mangano-manganic oxide. The early steel analysts precipitated the manganese with bromine only, and were in consequence compelled to wait many hours for a complete precipitation. Even when the present-day practice of adding ammonia (after the saturation with bromine) was adopted, it was at first by no means uncommon to let the precipitate await filtration for a very long time. Bromine with mercuric oxide, and hydrogen peroxide with ammonia, have also been used for precipitating the manganese.

Fixed alkaline salts, according to Meinecke, can be easily washed from the precipitate after digestion with ammoniacal ammonium chloride; this latter salt must then be washed out because of partial volatilization of the oxide of manganese in its presence. This injunction is most important in connection with the estimation of manganese in spiegels, etc., where the precipitate is very large, and very thorough washing causes it to pass through the filter. Eggertz used one per cent. hydrochloric acid and Meinecke very dilute nitric acid for washing.

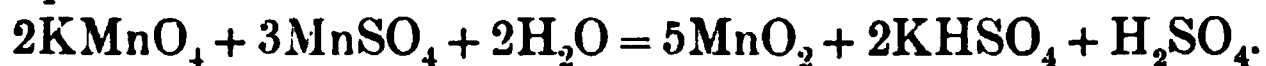
The question of the composition of the ignited precipitate has given rise to much discussion. This arose from Pickering's experiments, in which various  $\text{MnO}_2$ – $\text{MnO}$  compounds were ignited in an open platinum vessel over a bunsen flame, and were found to be variously oxygenated. Out of contact with reducing gases, a condition fulfilled by ignition at a muffle at a nearly white heat, the compound is

certainly  $\text{Mn}_3\text{O}_4$ , but an element of uncertainty is introduced when the precipitate is heated in a platinum vessel over a flame. The cause of such mischief is to be found in the permeation of the platinum by the reducing gases of the flame. This source of error is known to apply to other cases of ignition, notably that of zinc oxide and tetroxide of antimony.

This question of the uncertain composition of the ignited oxide of manganese gave considerable impetus to the precipitation of the manganese in the form of its double phosphate with ammonium, with final ignition to manganese pyrophosphate. This method has been occasionally appraised beyond its true worth, although there is no doubt that as processes go it is both accurate and useful.

Other gravimetric estimations of manganese are: (1) weighing as sulphate, in the ignition of which precaution must be taken against retention of water, and also against decomposition; (2) weighing as sulphide; and (3) weighing as hydrated peroxide, after electrolytic deposition from the sulphate, pyrophosphate, or from acetic and nitric acid solutions of the metal, such substances as acetone, chrome alum, alcohol, and ammonium acetate being added to facilitate the electrolysis. Carnot's precipitation and estimation of the manganese as a vanadate ( $2\text{MnO} \cdot \text{V}_2\text{O}_5$ ) belongs to the class of processes which might be useful, if not too expensive.

**The Volumetric Estimation of the Manganese** next calls for a short description. Guyard in 1863 suggested the titration of manganous solutions with standard solution of potassium permanganate, according to the equation:



He claimed also that this reaction separated many other metals from manganese; our experience points to the conclusion that in some cases these alleged separations are by no means exact. For highly maniferous material, however, Guyard's titration (or some modification of it), preceded by the separation of the iron, with or without filtration, is one of the most useful and exact processes when carried out in a faintly acid solution. The end of the reaction may be judged either by the formation of a tinge of colour, or by adding excess of the permanganate, filtering, and estimating the excess with a suitable reducing agent. In order to determine the formation of a precipitate corresponding precisely to the formula  $\text{MnO}_2$ , the titration is carried out in a hot solution, or in the presence of a metallic sulphate such as that of zinc; to effect the same purpose, the solution containing the manganese may be poured into the permanganate. Sometimes also the neutralized

solution of iron and manganese is poured into an alkaline solution of permanganate, in which case the iron is precipitated along with the manganese. Obviously chromium, if present, would interfere with this modification of the process.

A volumetric method of very limited application is that of the oxidation of the manganese to permanganic acid in nitric or nitro-sulphuric acid solutions by means of lead peroxide or red lead. The results are unreliable when more than small amounts of manganese are present. The permanganic acid formed may be estimated colorimetrically or volumetrically by means of a suitable reducing agent. In the former case the solution in nitric acid used for a colour carbon test may be boiled with red lead, and the manganese estimated on the same sample. In the latter case the permanganic acid may be titrated against solutions of mercurous nitrate, sodium arsenite, ammonium oxalate, sodium thiosulphate, ferrous sulphate, hydrogen peroxide or antimony trichloride.

When the oxidation to permanganic acid is effected by means of bismuth tetroxide or sodium bismuthate instead of red lead, *all* the manganese is readily oxidized, even when present in large amounts.

Another method consists in converting the manganese into manganic metaphosphate by boiling with sodium metaphosphate or phosphoric acid, together with an oxidizing reagent like lead peroxide or potassium chlorate, the violet solution being then either titrated or compared with standard colours.

The principle of the well-known Chlorate Process was discovered by Hannay, who refers to it as a means of separating iron and aluminium. This is one of the few points concerning which there has been no dispute. The most important differences of opinion have arisen over the composition of the precipitate. Stone did not consider it to be manganese dioxide; the amount of oxygen it contained was too small. Raymond, Troilus, and Mackintosh were of the exactly contrary opinion, but, in order to determine this fixed composition, stated that it was necessary to add the potassium chlorate in small portions at a time and alternately with strong nitric acid. Some operators recommend collection of the precipitate without any previous dilution, the filtration being followed by a washing with nitric acid, whilst others use weaker acid, add the chlorate all at once, dilute before filtering, and save acid by washing with water instead. Such amazing contradictions concerning apparently simple points in an experimental science do little credit to our philosophic sense.

As we do not propose to describe the Chlorate Process in the sequel,



the following points, concerning which there seems now to be general agreement, may with advantage be added here. The precipitate contains rather less oxygen than is demanded by the formula  $\text{MnO}_2$ , so that in assaying highly manganiferous materials, the titrating liquids should be standardized with a precipitate obtained from similar material containing manganese which has been most accurately determined. Small particles of potassium chlorate, mechanically occluded in the precipitate, are difficult to wash out; sodium chlorate is more soluble, and more easily decomposed in the oxidation of the manganese. Chrome steels are imperfectly decomposed, and the undissolved portion may introduce error through the attack of the acid-reducing liquids used for dissolving the manganese dioxide. The process is interfered with by the presence of lead, cobalt, bismuth, and phosphoric acid. Silicious ores, and slags may be more readily opened out for the process by the use of hydrofluoric acid. Finally, as the manganese is entirely precipitated, the chlorate process is sometimes useful as a preliminary to other volumetric operations in which small amounts of iron, accompanying the manganese dioxide, are of no serious moment.

Though by far the most extensively known, the chlorate process is by no means the only one depending on the conversion of a salt of manganese into the dioxide. According to various observers, this conversion can be accomplished with the following reagents:—Zinc oxide and bromine, mercuric oxide and bromine, sodium hydrate and iodine, bromine and ammonium or sodium hydrate, hydrogen peroxide and ammonia, bromine and calcium carbonate, and bleaching powder. Fusion with alkaline carbonates and subsequent reduction with alcohol has also been used. Some of these reagents yield precipitates corresponding to  $\text{Mn}_6\text{O}_{11}$ ; the formation of the true oxide is assisted and ensured in some methods, of which Pattinson's is the most widely known, by the addition of such salts as zinc chloride, ferric chloride, potash alum, and salts of calcium.

The only remaining processes of note are the precipitation of the manganese as oxalate with titration by permanganate; and the precipitation with ferri-cyanide, the resulting ferro-cyanide being estimated.

## THE GRAVIMETRIC ESTIMATION OF MANGANESE.

### **The Separation with Acetate and Weighing as $\text{Mn}_3\text{O}_4$ .**

The difficulty of the acetate separation, when it is followed by the gravimetric estimation of the manganese, does not consist so much in



keeping all the manganese in solution as in getting all the iron out. Dissolve 5 grams of the steel in hydrochloric acid and then oxidize the iron with a few c.c. of concentrated nitric acid. (The practice of dissolving in *nitric acid only* is not recommended, on account of the possibility of a small quantity of iron being left ultimately in solution through the agency of the nitrated carbon products. Tamm objects to the presence of this acid at all, as it may cause a little manganese to be precipitated as  $\text{Mn}_2\text{O}_3$  along with the iron; we have been unable to realize this danger in the numerous test analyses actually done). Dilute the solution, and then neutralize<sup>1</sup> it as far as possible without actually forming a permanent precipitate. Heat to boiling and precipitate with ammonium acetate made by neutralizing strong ammonia with strong acetic acid. The more perfect the neutralization of the solution has been previous to the heating and addition of the acetate, the less the amount of this reagent required for the precipitation of the iron; perfect neutralization demands less than 2 c.c. of acetate per gram of iron, but twice or thrice this quantity will cause no precipitation of manganese along with the iron. Make the boiled solution up to a litre, note the temperature, filter off half a litre through a fluted paper, taking care to put the first portion of the filtrate through the paper again, and again note the temperature of the filtrate.

In the following table, calculated from Kopp's numbers for the expansion of water, the first vertical column shows the temperature of the half-litre filtrate, the top horizontal column the litre temperature, and the intersection of a pair shows the volume which the half-litre would occupy at the litre temperature. This figure, divided by 1000,

500 c.c. at	Equivalent at							
	65°.	70°.	75°.	80°.	85°.	90°.	95°.	100°.
60° C.	501·4	502·8	504·4	506·0	507·6	509·4	511·2	513·2
65°	—	501·5	503·1	504·6	506·3	508·1	509·9	511·3
70°	—	—	501·6	503·4	504·8	506·6	508·4	510·3
75°	—	—	—	501·6	503·2	505·0	506·8	508·8
80°	—	—	—	—	501·7	503·4	505·3	507·2
85°	—	—	—	—	—	501·8	503·6	505·6
90°	—	—	—	—	—	—	501·9	503·8
95°	—	—	—	—	—	—	—	502·0

<sup>1</sup> There is considerable ambiguity in the use of the term "neutralize." In this connection it does not merely mean the actual neutralization of the free acid, but the formation of an oxychloride of iron. This point is treated more fully under the estimation of nickel, page 67.

shows the proportion of the weight of the sample originally taken which is being used for the actual determination of the manganese. The table is drawn up on the assumption that the solution expands just as water ; moreover, no account is taken during the fractional filtration of the actual volume of the precipitate. Neither of these corrections is necessary.

Cool the filtrate, add a few c.c. of bromine and as much ammonia as makes the solution smell distinctly, but not more ; boil, filter, and wash. If the later washings carry small quantities of the precipitate through, as they are apt to in the assay of manganese alloys, where the precipitate is very large, even when smaller amounts of the sample are weighed off in the first instance, these should be re-passed through a small, closely-made pulp filter, which is ignited in the crucible intended for the reception of the main precipitate. Ignite in a muffle at a bright red heat. For very exact work, the precipitate after weighing should always be examined for ferric oxide, silica, and alumina, and also for the oxides of nickel and copper if these metals exist in the original sample. For the determination of ferric oxide (the most important impurity), the mangano-manganic oxide is dissolved in hydrochloric acid, the solution evaporated nearly to dryness, filtered from any silica that may be present, and solution of potassium thiocyanate added. The red colour obtained is then matched by that obtained from a known amount of a slightly acid solution of ferric oxide similarly treated with the thiocyanate. Not more than a milligram of ferric oxide should ever be found.

## RAPID VOLUMETRIC PROCESSES.

### **The Red Lead Process.**

Dissolve one gram of steel in 100 c.c. of a mixture made from

1500 c.c. water,  
500 c.c. nitric acid (s.g. 1.42),  
70 c.c. sulphuric acid,

and when all the brown fumes are boiled away, add 3 or 4 grams of lead peroxide or red lead,<sup>1</sup> boil for a few minutes, add another lot of red lead, boil, add 200 c.c. of cold distilled water briskly, and filter

<sup>1</sup> As commercial lead peroxide is manufactured by treating alkaline solutions with chlorine made from manganese dioxide, it nearly always gives a pink colour when boiled with the acid mixture alone. Red lead free from manganese is, however, easily obtainable.

through asbestos. Wash by decantation until the washings are free from colour, add an excess of ferrous sulphate of known strength, and titrate with permanganate which has been standardized against a steel whose manganese has been carefully estimated gravimetrically.

The process admits of a large number of samples being carried through simultaneously, and is accurate if the manganese present is less than one per cent. If the manganese reaches one per cent. the results may be as much low as 0.03 or 0.04 per cent. (or even more if the carbon is also very high); samples containing more manganese than this should be assayed on one half or a quarter of a gram, so as to have less than one centigram of manganese actually present. Aluminium, molybdenum, and tungsten do not influence the result; copper and nickel exert no further influence than may be due to the colour of their solutions in the filtrate.

Chromium, if present, is oxidized to chromic acid, and this interferes with the subsequent titration more or less according to the substance used for titrating. Ferrous sulphate is inadmissible in this case: it reduces chromic acid almost as readily as it does permanganate when these two are present together. The use of ammonium oxalate for the titration, however, gives very satisfactory results. The most convenient and accurate mode of procedure is as follows: gauge the approximate percentage of manganese in the sample from the colour of the filtrate, run from a burette into the heated ( $70^{\circ}$ – $80^{\circ}$  C.) solution as much of the oxalate as will certainly destroy the colour<sup>1</sup> without leaving a great excess, and titrate the excess as quickly as possible with standard permanganate. The colour changes from lemon to orange when only a trace of permanganate is in excess. The volume of solution titrated should be about 400 c.c. A large excess of oxalate should be avoided, as it slowly reduces the chromic acid. The chromic acid may now be titrated with ferrous sulphate for the estimation of the chromium, but the results are seriously low if several per cents. are present, because part of the chromium remains in the residue.

The results obtained by this process when applied to iron to which gradually increasing amounts of manganese are added, are very curious. Assuming that one gram of metal is operated upon, the increasing amounts of manganese give rise to increasing and proportional amounts of permanganate up to one per cent. manganese; beyond this, and up to about four and a half per cent., the permanganate obtained also increases, but not proportionally. Beyond this percentage the perman-

<sup>1</sup> The reaction between the oxalate and permanganate is much speedier if a little manganous sulphate is also added.

ganate formed falls off, until, when the manganese approaches the amount met with in rich samples of ferro-manganese, there is no final indication of manganese in the filtrate at all unless very large amounts of red lead are used. If the results of such a series of experiments are set out in the form of a curve whose ordinates represent percentages of manganese, and abscissae amounts of permanganate formed, it follows that the curve will cut the horizontal axis at two points considerably distant from each other. We have thus the possibility of getting the same manganese contents out of two different materials which actually contain widely-different amounts of this metal. We have known such contingencies to actually arise in practice, material of which nothing was known, but which actually contained 13 per cent. of manganese being found by the process to contain 0.40 per cent. This error is one which need never be committed twice if it has once been observed that with such highly manganiferous material the first addition of red lead causes a momentary pinkness, which soon disappears, leaving a very brown residue.

#### **The Bismuthate Process.**

The special reagent required—sodium bismuthate—may be bought at about twenty shillings a pound. The following are Reddrop and Ramage's instructions for preparing bismuthate of such strength that one gram has an oxidizing power equal to fifty or sixty c.c. decinormal permanganate.

Heat twenty parts of caustic soda nearly to redness in an iron crucible, and add, in small quantities at a time, ten parts of basic bismuth nitrate which has been dried in a water oven. Two parts of sodium peroxide are then added and the brownish yellow fused mass is poured out on an iron plate to cool; when cold it is broken up in a mortar, extracted with water, and collected on an asbestos filter. The residue after being washed four or five times by decantation is dried in the water oven, then ground and passed through a fine sieve. Its oxidizing power is determined by adding half a gram to a measured amount of ferrous sulphate or hydrogen peroxide, and titrating the excess with decinormal permanganate.

To make an estimation dissolve 1.1 grams of steel in 35 c.c. of nitric acid of 1.20 specific gravity. After cooling somewhat add bismuthate, a little at a time, until a permanganate colour persists on boiling or becomes decomposed to manganic oxide. Add a small excess of sulphurous acid, hydrogen peroxide, or (manganese-free) ferrous sulphate, and cool. To the quite cold and almost colourless

solution add a gram or so of sodium bismuthate, shake well and filter into a clean flask through such an asbestos arrangement as is used for collecting the carbonaceous residue (page 14). Wash with three per cent. nitric acid until the washings are colourless, and then add an excess of ferrous ammonium sulphate and go back with permanganate.

$$1 \text{ c.c. } \frac{N}{10} \text{ KMnO}_4 = \cdot 10 \text{ per cent. manganese.}$$

The above process is a modified form of that given by Reddrop and Ramage (*J.C.S.* lxvii. 268). Bismuthate is added to the hot solution to destroy the organic matter and also to provide a more stable end reaction in the titration; this operation is an important one when very high carbon steels, and particularly white irons, are being assayed. We prefer to make the titration with ferrous sulphate and not hydrogen peroxide, because the latter can react with ferric nitrate solutions, and shows increasing amounts of manganese as increasing amounts of peroxide are used. This explains why filtering into hydrogen peroxide always gives higher results than filtering into an empty flask and then adding the peroxide. Ferrous sulphate is quite free from this objection, and can be safely used in nitric acid solutions if the titration with permanganate is not delayed. These differences between Messrs. Reddrop and Ramage and ourselves are fully discussed in the *Chemical News*, lxxxiv. and lxxxv.

The solution to be oxidized should contain not less than one half its volume of 1·20 nitric acid. Hydrochloric acid must not, but sulphuric acid up to normal strength may be present.

In the modified process just given any chromium in the steel would be oxidized to chromic acid when the bismuthate was added to the hot solution. Care must then be taken that enough sulphurous acid is added to reduce it again to chromic oxide before the solution is cooled and the estimation proceeded with. In order to minimize the formation of chromic acid when the estimation is being made, the solution should be as cold, and the oxidation and filtration completed as quickly, as possible. On adding bismuthate, shaking vigorously for a few seconds and filtering rapidly, we obtained 0·52 per cent. manganese from a steel containing 0·50 per cent. manganese and 3·00 per cent. chromium. After standing in contact with the bismuthate for five minutes the result was 0·55 per cent., and after standing ten minutes 0·57 per cent. manganese. Steels containing chromium are not always soluble in nitric acid, but the most obstinate of such cases can be dealt with by digesting the sample with 10 c.c. (1 to 3)

sulphuric acid until it is decomposed, and then adding nitric acid and finishing as usual.

Tungsten does not interfere (see estimation of manganese in ferro-tungsten); neither do molybdenum, vanadium, nor titanium, if ferrous sulphate (and not hydrogen peroxide) is used for titrating the permanganate formed. The only evidence in the titration that any of these elements are present occurs with vanadium, when on adding the excess of ferrous sulphate the hypovanadate colour appears. When the excess of ferrous sulphate has been decomposed and the added permanganate is re-oxidizing the hypovanadate to the pentoxide, the end point is not so sharp and clear as when vanadium is absent, but the uncertainty need never involve more than one or, at most, two tenths of a c.c. decinormal permanganate.

Where economy is a great consideration one may proceed with series of every-day steels in the following manner. Pass two samples through the same filter, then pour on to the bismuthate-coated filter a sample which has been merely dissolved and cooled or to which a bare excess of bismuthate has been added. A funnel large enough to hold all the ferric solution should be used so that the bismuthate may be evenly diffused through the liquid by stirring with a small glass rod. The filtration should not be accelerated beyond what is necessary to cause the solution to pass rapidly in drops. The results are accurate.

By oxidizing in the flask.	By passing only through the filter.
0.62	0.60
2.29	2.25
.58	.58
.68	.67
.09	.10

The most important feature of the Bismuthate Process is the oxidation to permanganate *in the cold*. This should not be regarded as an incident merely which adds to the convenience of the operation; it is *the* fact on which the success of the method with large amounts of manganese depends. It may be stated generally that any reagent capable of effecting the transformation to permanganate only when aided by heat is not suitable for the estimation of large amounts of manganese, and any reagent which can rapidly effect the transformation in the cold is. The reason for this distinction is that permanganate solutions are readily decomposed on heating, particularly if manganous salts are present, so that to be fairly successful with very moderate amounts of manganese an oxidation in heated solutions must be

instantaneous. When a solution of ferro-manganese is oxidized by successive small amounts of lead peroxide, it is clearly seen that permanganate is formed and then almost immediately decomposed by the unoxidized manganous nitrate.

Fairly strong nitric acid solutions are required for cold oxidations because increasing acidity retards the formation of manganese dioxide by mutual decomposition, as on p. 28. It is an easy matter if the acidity is neglected to have manganic oxide formed and filtered off with the excess of bismuthate when dealing with manganese alloys; and therefore if any doubt exists the filter should be re-boiled with nitric and sulphurous acids, and after cooling re-oxidized.

## SULPHUR.

### PRELIMINARY SUMMARY.

**Gravimetric Estimation.**—Nearly all the means of estimating sulphur in minerals and metallurgical products depend either on the oxidation of the sulphur to sulphuric acid or its liberation as sulphuretted hydrogen: a combination of the two, *i.e.* oxidation of the liberated sulphuretted hydrogen to sulphuric acid was in use very early in the practice of steel analysis. These two groups may be further sub-divided into volumetric and gravimetric processes. The former are confined to the estimation of evolved sulphuretted hydrogen: there are no volumetric processes for the estimation of such small amounts of sulphuric acid as are got from steel.

**Dissolving.**—In order to oxidize the sulphur to sulphuric acid in the presence of iron the borings are treated with bromine, bromine and acids, hydrochloric acid and an alkaline chlorate, dilute nitric acid, or a mixture of nitric and hydrochloric acids added singly or as aqua regia. The last named are most extensively used.

Solution of the steel in aqua regia, elimination of nitric acid and precipitation of barium sulphate from the solution of ferric chloride is frequently referred to as the standard process. The procedure has, however, been modified at almost every step in order to eliminate some real or imaginary error, and the impression left on the mind after reading what various authorities have to say is, that the standard process is by no means a perfect one.

When iron is dissolved in nitric acid it is said that loss occurs through



the escape of both sulphur and sulphuretted hydrogen. And according to Lunge, even when aqua regia is used to oxidize ferrous sulphide a portion escapes as sulphuretted hydrogen: the separate addition of the acids minimizes this loss.

*Evaporation.*—The solution of the metal is evaporated to dryness and baked, ostensibly for the purpose of dehydrating the silica so that it may be filtered off. But as dissolved silica is not carried down by barium sulphate, and as it could be removed by evaporation with hydrofluoric and sulphuric acids even if it were, there must be some other reason for so lengthy a procedure. One reason is the elimination of nitrates, which are more favourable to the inclusion of impurities by the barium sulphate than chlorides are; and another is the destruction of the nitrated (combined) carbon compounds, which are always present when steel is dissolved in nitric or nitro-hydrochloric acid. For both purposes it is necessary to bake the dried mass on a hot plate<sup>1</sup> or sand bath, and in order that no sulphuric acid may be lost by the decomposition of the basic ferric sulphate, it is usual and necessary, but not the invariable practice, to add a pinch of some alkaline salt, so that the sulphuric acid may be combined in a non-volatile form.

*Precipitating.*—The dried mass is re-dissolved in hydrochloric acid. From this point the various instructions as to the acidity, etc., of the solution to which the barium chloride is added are very confusing. About thirty years ago, on the publication of a method in which the barium sulphate was precipitated from a distinctly acid solution of ferric chloride, the best-informed analysts believed, and said, that the presence of free hydrochloric retarded, if it did not altogether prevent, the precipitation of barium sulphate, and that the iron solutions should be neutralized as far as possible with some alkali before adding the barium chloride. The only reason which can be given for the continued retention of this troublesome detail is the mere statement of persons who were expected to know, and the apathy of those whose business it should be to test 'authoritative' statements for themselves. Another tradition was, that the ferric chloride solution should be largely diluted before precipitating the barium sulphate.

Whether, in keeping with the above views, the free acid was got rid of by evaporating until the surface of the ferric chloride began to skin over, or by adding ammonia or other alkali, the tendency and very largely the practice was to overstep the formation of normal ferric chloride and get the more or less dark red solution of oxychloride. Now a very dilute solution of ferric oxychloride, particularly if heated,

<sup>1</sup> Snelus is credited with having first introduced the hot plate at Dowlais.



is readily precipitated by an alkaline sulphate, and under these circumstances it is easy to get a basic ferric salt mixed with the barium sulphate. These practical difficulties for the most part may now be avoided, since the practice of some of the earlier iron-analysts of precipitating from a fairly concentrated and moderately acid solution has been revived and shown, by Archbutt, to be actually more favourable to complete precipitation.

It appears, however, particularly when the amount of sulphur is large, that the tendency of iron to be carried down by barium sulphate cannot be quite eliminated by having a little free hydrochloric acid present, and various expedients have been adopted for keeping it up. They are: the addition of oxalic, tartaric, or citric acid; reduction of the iron to the ferrous condition with zinc, sodium amalgam, or stannous chloride; precipitation of the iron with an excess of ammonia and of the sulphur from the acidified filtrate; or precipitation with ammonia, addition of barium chloride to form barium sulphate, and then hydrochloric acid to re-dissolve the ferric hydrate. As an aid to the precipitation and collection of small amounts of barium sulphate, silver nitrate or a known amount of sulphuric acid, is sometimes added. The silver chloride due to the former is washed from the filter with ammonia, and the barium sulphate due to the latter is finally deducted.

Whether or not all the sulphuric acid is precipitated from ferric chloride solutions depends on the dilution, acidity, temperature, and other variable circumstances. But the precipitate has a decided tendency to occlude impurities; compounds of sodium, potassium, copper, magnesium, and barium, as well as iron, having been observed in the ignited barium sulphate.

*Ignition.*—The ignited precipitate may be affected by reducing gases permeating the platinum crucible when heated over a naked flame, or by the carbon of the paper however the ignition is made; the separate ignition of the paper and so small and powdery a precipitate being practically impossible. It is said that if the filter be ignited apex upwards the reduction of the sulphate is avoided or greatly lessened. It has also been suggested that the filter should be ignited first at a low temperature and then calcined in a strongly oxidizing atmosphere. But barium sulphate, as well as calcium or lead (sulphate), is decomposed at high temperatures, and therefore no correction of the reduced sulphate seems so satisfactory as treatment with sulphuric acid or sulphuric acid and bromine and re-ignition at a moderate temperature.

It is very difficult to make a correction for a precipitate which on ignition shows the presence of ferric oxide. If the impurity, however

reckoned, makes a serious difference the assay had better be repeated. If the ferric oxide is due to basic ferric sulphate having been carried down the correction required would be positive, but if it were due to imperfect washing of the filter the correction would be negative.

The numerous possibilities of error surrounding the estimation of sulphur are typical of those met with elsewhere. The errors are of course not all in the same direction, and results obtained by seemingly crude processes come much nearer the truth than might be imagined. The conditions of modern steel works' practice hardly leave time for the thought of, much less the practice of, the means by which scientifically accurate results are obtainable. Nevertheless, it is well that one should know what the minor errors incidental to making every-day control tests are; one can then appreciate Fresenius' statement that "the analysis of cast-iron is one of the most difficult problems of analytical chemistry."

The remaining gravimetric methods need only be enumerated :

1. Decomposition of the borings with ferric or cuprammonium chloride solution, oxidation of the carbonaceous residue, which contains all the sulphur (chiefly in combination with manganese), by such reagents as are used for the direct attack of the steels, and precipitation with barium chloride.

2. (a) Evolution as sulphuretted hydrogen into solutions of zinc, potash, permanganate, silver nitrate, mercuric cyanide, hydrogen peroxide, bromine and hydrochloric acid, and oxidation when necessary by such reagents as have already been enumerated.

(b) Absorption by neutral or alkaline solutions of lead, oxidation to and weighing as lead sulphate.

(c) Absorption in alkaline cadmium solutions, the sulphide being dried and weighed; or the precipitated sulphide being added to copper sulphate and the resulting sulphide ignited to cupric oxide. The direct precipitation of copper by sulphuretted hydrogen, although extensively practised, is objectionable, as phosphoretted hydrogen also decomposes cupric sulphate solutions.

(d) As c, but using other metallic salts such as silver nitrate, the sulphide or some other compound of the metal being weighed.

3. Fusion of the finely divided metal with sodium peroxide or with a mixture of magnesia and caustic soda, dissolving out the alkaline sulphates and precipitating as usual. Or addition of a few grams of an alkaline salt to the acid solution of the metal, ignition of the dried mass, and dissolving out alkaline sulphate as before.

From what has already been said it might be expected that results obtained by the direct fusion of the metal would be higher than those obtained by oxidation with acids. This is found to be so, and irons may be met with which yield the full percentage of sulphur only to some such method.

**The Volumetric Estimations** all depend on the conversion of sulphur to sulphuretted hydrogen. This is generally accomplished by treating with an acid, but heating the powdered metal in a current of hydrogen, or hydrogen and carbon dioxide, also forms sulphuretted hydrogen, and has been suggested for the assay of metals, fuels, or slags.

The earlier forms of the evolution process were supported by the impression that on digesting the metal with acid *all* the sulphur was evolved as sulphuretted hydrogen. The operations were so simple and speedy that nothing but very gross and obvious failures, and a seemingly endless number of modifications of a contradictory kind could have prevented its altogether superseding the ordinary aqua regia process. The following statements include the various suggestions made.

*Evolving the Sulphur.* — Both hydrochloric and sulphuric acid have been used for attacking the steel; the former is generally preferred. Dilute acids are sometimes used, but in order to avoid the interference of copper and such elements as tend to form insoluble sulphides, and also in order to evolve all the sulphur as sulphuretted hydrogen, it is better to use the strong acid. Sulphuric acid alone is said to give low results, but a mixture of hydrochloric and sulphuric dissolves the iron more readily than either acid used singly.

It is admitted nowadays that sulphur is apt to be left in the evolution flask. That this is due to sulphuretted hydrogen becoming oxidized by the atmosphere of the flask through the agency of a little ferric chloride is an insufficient explanation. To avoid this oxidation, however, the evolution is occasionally accomplished in an atmosphere of hydrogen, nitrogen, or carbonic acid; or zinc, tin, or stannous chloride are dissolved along with the sample. Tin, zinc, or stannous chloride are said to transform any evolved sulphurous acid into sulphuretted hydrogen,<sup>1</sup> in addition to preventing the formation of ferric chloride.

<sup>1</sup> At one time we proposed to hurry the decomposition of some ferro-silicon alloys by adding hydrofluoric acid when the evolution of sulphuretted hydrogen had slackened. The invigorated attack of the alloy was accompanied by a very copious evolution of sulphuretted hydrogen, and much more sulphur was registered than could be found in the alloy by gravimetric methods. This was accounted for eventually by the fact that any metal evolving hydrogen when attacked with acid evolves sulphuretted hydrogen also, if commercial hydrofluoric acid is added; the reason being that sulphuric acid, which is always present, is thereby reduced.

*Absorbing Sulphuretted Hydrogen.*—The sulphur evolved and that recovered by digesting the residue with aqua regia, and precipitating as barium sulphate, should always have equalled the amount obtainable by the standard gravimetric process, whatever class of material was being dealt with. This was a one-time axiom. But it appears now that the sum total of sulphur found in these two ways ought frequently to have been less than the amount actually present. This is so because Phillips has discovered that a portion of the sulphur, the amount varying with the class of material, is evolved as an organic sulphur compound (methyl sulphide and mercaptan), which is neither oxidized nor precipitated by the ordinary reagents, and is only transformed to sulphuretted hydrogen when passed through a hot tube. This important addition to our knowledge helps to explain some anomalies.<sup>1</sup>

Some experiments by Matthewman (West of Scotland Iron and Steel Institute, Session 1895-96) elucidate a point in the evolution process which is rarely alluded to. He found that the sulphur evolved from pig iron and high carbon steel samples was greater the more rapid the evolution, and that the highest result was obtained when the rate of evolution was so rapid as almost to project the absorbing liquid from the vessel, and certainly so rapid that a portion of the sulphuretted hydrogen escaped absorption. A pig iron containing 0·15 per cent. sulphur gave the following results :

Rate of Evolution.	Sulphur per cent.
Extremely rapid, - - -	0·132
Rapid, - - -	·122
Usual rate of evolution, - -	·092
Slow, - - -	·076
Extremely slow, - - -	·049
Do., - - -	·036

The varying results have been linked with the fact mentioned in the last paragraph by the suggestion that slow evolution is more favourable to the formation of sulpho-carbon compounds than rapid evolution, but at present no experimental evidence of a convincing kind has been produced in support of this view.

The above table explains why sievings which dissolve very readily give higher results by the evolution process than the coarse pieces,

<sup>1</sup> Passing the gases through a hot tube will also decompose evolved hydrocarbons, whose interference with the subsequent estimation of sulphur has been pointed out in journals, but generally disregarded in text books.

although no difference can be detected by the most rigorous oxidation and gravimetric estimation. Assuming that local impurities of a sulphurous nature do not concentrate either in the fine or coarse pieces, it is an advantage to follow Ledebur's practice of sieving out the amount required for the assay.<sup>1</sup>

The more important reagents used for absorbing the sulphuretted hydrogen, and the modes of completing the estimation, are :

1. Absorption by solution of caustic alkali, cadmium, zinc, arsenic, or iodized potassic iodide, and titration with iodine or thiosulphate.
2. Absorption in a neutral solution of a metallic salt, and titration of the liberated acid.
3. Absorption in caustic alkali, addition to an acid solution of a reducible salt ( $\text{Fe}_2\text{O}_3$ ), and titration of the lower oxide ( $\text{FeO}$ ) formed
4. Titration of the alkaline sulphide with a solution of an easily precipitated metal [ $\text{Pb}(\text{NO}_3)_2$ ].
5. Absorption in solution of a metallic salt ( $\text{Pb}$ ,  $\text{Cu}$ ,  $\text{As}$ ), and measuring of the precipitated sulphide after whirling in a centrifugal machine ; or assaying the undecomposed filtrate.
6. Passing the sulphuretted hydrogen through a series of bulbs containing equal volumes of a standard [ $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  or  $\text{AgNO}_3$ ] solution. As no two bulbs are discoloured simultaneously the result is arrived at by counting the number of bulbs affected.
7. Comparing the colour of a metallic plate, or calico soaked with a metallic salt, or a solution of a metallic salt over, or through, or into which the sulphuretted hydrogen has passed, with standards.

### GRAVIMETRIC ESTIMATION OF SULPHUR.

To five grams of steel add 20 c.c. nitric acid (1.42), and then 25 c.c. concentrated hydrochloric acid, a little at a time. The reaction should not be hurried, but a capacious vessel of cold water should be handy in order to moderate any violent reaction which threatens to overflow the beaker. When dissolved add about half a gram of potassium nitrate crystals, and boil briskly with the cover on until the dark clear solution shows a turbidity ; the solution does not spirt until this point is reached, but afterwards it will. The evaporation may be completed either by drawing the beaker to the edge of the hot plate and heating it with the cover off just strongly enough to keep the semi-solid mass bubbling ;

<sup>1</sup> Ledebur is of opinion that sievings are richer in sulphur than the coarse pieces.

or by passing a strap round the beaker (see p. 23) and keeping it in rapid motion over a bunsen until the mass solidifies.

The dried mass, after heating very strongly for half an hour or so, is cooled and digested with 20 c.c. hydrochloric acid until everything is dissolved. The solution is then re-evaporated until a skin just begins to form on the surface, or until, on whirling the beaker, the solution at once crystallises on the sides. If this evaporation is made at a comparatively low temperature, small drops of the solution rise up the sides of the beaker and fall back again. This very marked instance of a solution "moving itself aright" continues until just before the skin forms. It needs some judgment to arrange the formation of the skin in an easily distinguishable way; after the point is reached add 4 c.c. hydrochloric acid, dilute with two or three times its volume of hot water, pass through a small filter to eliminate silica, add barium chloride in excess to the filtrate, and allow to stand. Archbutt found that the precipitation of barium sulphate from concentrated and somewhat acid solutions of ferric chloride was complete in two hours or less; it is generally convenient, however, to precipitate in the evening and allow to stand overnight. The collected barium sulphate is washed with cold and very dilute hydrochloric acid, so as to avoid the formation of basic ferric salts, and then ignited and weighed.

Each fresh supply of reagents must be tested for sulphur. Some difference of opinion exists as to how this should be done; but the mere evaporation of the mixed acids with a pinch of an alkaline salt or Swedish bar iron is certainly not satisfactory. A blank test should always be made under conditions as nearly like those of the actual estimation as possible, the object being to determine not absolutely how much of a particular impurity the reagents contain, but the amount of impurity affecting the estimation.

If a steel known to be free from sulphur or containing only a negligible amount can be obtained the blank is best determined by assaying it. Otherwise two and a half and five grams of any steel are dissolved in equal amounts of the acids and the usual operations performed. From the amounts of barium sulphate obtained the 'blank' is calculated by deducting the weight of the precipitate obtained from the five grams from twice the weight of the precipitate obtained from the two and a half grams. Or if A and B represent the respective amounts of barium sulphate obtained then

$$\begin{aligned} A &= \text{BaSO}_4 \text{ due to 5 grams of steel + reagents.} \\ 2B &= \text{,, ,, ,, ,, + double amount of reagents.} \\ \therefore 2B - A &= \text{BaSO}_4 \text{ due to reagents.} \end{aligned}$$

Where the precipitate is slightly soluble in the mother liquor or the wash waters, the presence of a small amount of a particular impurity in the reagents may be an advantage, if the blank test is made so as to reproduce the precise conditions for solubility, etc., of the assay; in fact it enables the defect inherent in the method to be eliminated almost entirely.

### VOLUMETRIC ESTIMATION OF SULPHUR.

In a busy steel works' laboratory where the gravimetric estimation is considered too slow for general use many of the refinements mentioned in the preceding summary, such as passing the evolved gases through a heated tube before absorption, are altogether neglected. The danger of this neglect is recognized and partly met by determining the strength of the standard solution against similar material to that being assayed and using the different factors calculated from the known amount of sulphur present according as the sample is pig iron, chilled iron, steel, or what not.

The solutions required for the following process are :

**For absorbing.**—Dissolve twenty grams of pure zinc in hydrochloric acid, add ammonia until a decided precipitate forms, redissolve it with acetic acid, and make up with water to a litre. Each absorption flask should contain about 100 c.c. of this solution.

**For titrating.**—A decinormal solution of iodine may be used, or one containing 7.94 grams iodine per litre; in the latter case each c.c. is equivalent to 0.001 grams of sulphur. The thiosulphate should correspond with the iodine, and the starch liquor should be in good condition.

A suitable form of apparatus is shown in Fig. 8. From two to ten grams of metal according to its supposed percentage of sulphur are weighed into the flask, the stopper inserted and 50 c.c. of concentrated hydrochloric acid mixed with 50 c.c. hot water passed into the flask through the small funnel shown on the left-hand side of the figure. Water is set going through the condenser and heat applied to the flask. When all is dissolved the small funnel is removed, a lead acetate wash-bottle attached, the screwcock opened, and the apparatus swept out with air so as to carry all the sulphuretted hydrogen into the absorption vessels. To the first absorption flask (which alone need be considered if the second is still clear), add an excess of iodine and shake a minute or so in order to promote decomposition of the zinc sulphide. Add 2 c.c. starch liquor and then thio-



sulphate until the solution at first green becomes clearly blue and finally colourless. The percentage of sulphur is calculated from the amount of iodine actually used, its value having been determined as aforesaid by known material similar to that being assayed.

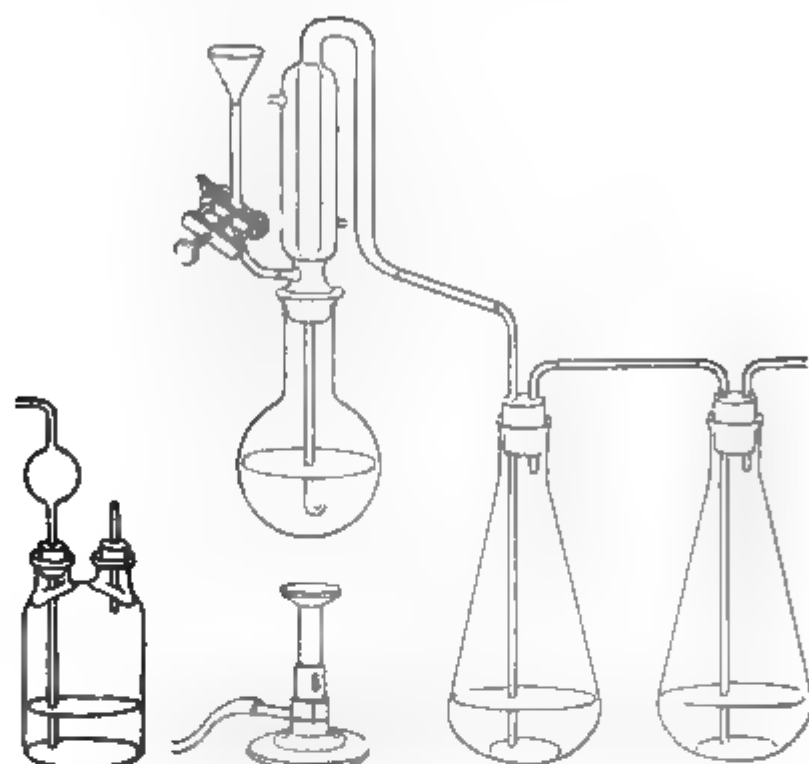


FIG. 8.

Schulte has examined various materials with respect to the proportion of sulphur evolved in organic combination and needing a hot-tube to transform it to sulphuretted hydrogen. With white irons the proportion varied from one to twelve per cent., and with spiegeleisen from seven to fifty-two per cent. With certain kinds of pig iron the proportion may be even greater, but in the bulk of work the laboratory has to deal with, *i.e.* mild Siemens-Martin and Bessemer steels, the proportion is comparatively insignificant.

## PHOSPHORUS

### PRELIMINARY SUMMARY.

The number of the papers in the various technical and scientific journals on the estimation of phosphorus in metallurgical materials outnumber those relating to the estimation of any other element. In a few pages it is possible to refer only to the more important or



interesting processes and to consider the one or two which, variously modified, are now almost universally used.

**The Separation of Phosphorus from Iron** may be accomplished :

1. By boiling neutral solutions of ferrous or ferric oxide as circumstances require, with silver nitrate, a metallic acetate, antimonie chloride ; or dissolving the material in nitric acid along with tin. In each case the phosphorus is precipitated.
2. By precipitating the iron with ferro-cyanide.
3. By dissolving, and igniting the evaporated residue with alkaline salts, or at once igniting the borings with a strong oxidising mixture (*e.g.* the tribasic mixture) and leaching out the soluble alkaline phosphate.
4. By heating the metal with a neutral solution of potassio-cupric chloride : the carbonaceous residue contains all the phosphorus, but no arsenic.

None of the above processes have been extensively practised, during recent times, in the analysis of steel-making materials, but it is interesting to recall the fact that in some cases they were proposed for that special purpose, and were said to be superior to others which have since become very popular.

The separation of phosphorus from the bulk of iron as basic ferric phosphate is a well-known and sometimes invaluable device. It is accomplished by transforming the iron to the ferrous state, reforming or adding a little ferric iron, and precipitating the peroxidised portion by means of ammonia, ammonium carbonate, or an emulsion of the hydrate or carbonate of calcium. It is sometimes an advantage to keep all the iron in the ferrous state, to add a little alum, and throw down a basic aluminic phosphate in the same way as before. In this separation the aim should be to make the phosphoric acid itself effect the precipitation as far as possible. In relation to the estimation of phosphorus in irons the above separation has been distinguished by the term, 'acetate process.'

**Precipitation with Magnesia.**—The separation as basic ferric phosphate and subsequent precipitation with magnesia is one of the earliest recorded methods for estimating phosphorus in irons. It was the custom, however, to separate the remaining iron completely with ammonium sulphide, and to precipitate the phosphorus from the filtrate ; although later the practice was to keep up the iron with tartaric acid, or tartaric acid and alcohol. But Warrington pointed out that a somewhat insoluble crystalline tartrate of magnesia frequently contaminated the precipitated ammonium magnesium phosphate, and he suggested the

substitution of citric acid. It is said also that in the joint presence of aluminium and tartaric acid phosphorus is not precipitated from an alkaline liquid by magnesia.

Since the conditions under which phosphorus is completely precipitated by nitric acid solutions of ammonium molybdate have become better understood, the molybdate-magnesia is equally as much if not more used than the acetate-magnesia process. There are methods which combine the two—i.e. an acetate-molybdate-magnesia process—on the assumption that in the presence of very large amounts of iron all the phosphorus is not precipitated by the molybdate reagent. But in any form the final precipitation with magnesia is not well adapted to the requirements of a steel-works' laboratory. The operations are too lengthy in comparison with the direct precipitation and estimation as phospho-molybdate, and, moreover, the ignited pyrophosphate multiplies the small amount of phosphorus looked for by 3.6 only.

The following imperfect summary is made mostly from papers dealing with the estimation of large amounts of phosphorus. Persons especially interested in finding out the best proportions of citrate and ammonia, excess of magnesia mixture, concentration of solution, alkalinity, influence of various alkaline salts, modes of correcting for phosphoric acid lost on ignition, and so forth, should consult the bibliography.

Dissolved silica has a tendency to carry down both iron and alumina from citrate solution; it should therefore always be removed by evaporation or otherwise.

Magnesia mixture should not be made from the sulphate, as it is partially deposited as such along with the double phosphate, and it should be added in drops. The presence of citric acid is desirable in any case in order to prevent the co-precipitation of magnesia, and to clear up a small precipitate of ferric phosphate, which is sometimes seen on dissolving phospho-molybdate in ammonia. Heating the two solutions before mixing is also favourable to the purity of the precipitate. The precipitation is complete in two hours, but it may be hastened by shaking, by stirring paper pulp into the liquid, or rubbing the sides of the beaker with a cropped leather. The precipitate is quite insoluble in strongly-ammoniacal solutions containing an excess of magnesia, but it is not always strictly the magnesium ammonium phosphate. It should be washed with dilute ammonia or a mixture of ammonia and alcohol.

Precipitate and paper need not be ignited separately if the loosely adherent portion be shaken out into the crucible. Any molybdic acid

present when a preliminary precipitation as phospho-molybdate has been made can be eliminated by strong ignition. Strong ignition, however, volatilizes some phosphoric anhydride, unless the moist precipitate was exactly the magnesium ammonium phosphate, through the intermediate formation of a meta-phosphate; but a coating of magnesia on the lid of the crucible retains some phosphoric anhydride and minimizes the error. The ignition is best made at a low temperature until the precipitate becomes white and then at higher temperatures. Precipitates which are obstinately black may be heated with ammonium nitrate. Reheating with strong sulphuric acid and weighing as pyro-sulpho-phosphate, has been recommended; the pyro-sulpho-phosphate multiplied by 0.470 equals  $P_2O_5$ .

**Precipitation with Molybdate.**—The advantages of the direct precipitation as phospho-molybdate are: that it is not seriously hampered by the presence of large amounts of iron, and that it provides a precipitate under easily obtainable conditions which is of constant composition and weighs sixty-three times more than the phosphorus looked for. This latter circumstance greatly enhances the accuracy of the process when very small amounts of phosphorus are being estimated, and probably also accounts for its vigorous survival through a period when it was neither properly understood nor unanimously approved, in its more important points, by those who practised it.

**Dissolving.**—The prevailing notion of the part played by the nitrated carbon compounds existing in solution has greatly influenced the *modus operandi* after the steel has been dissolved in dilute nitric acid. The imperfect precipitation of phosphorus was ascribed to these organic compounds when evaporation and baking with or without suitable oxidising reagents was not resorted to. Now, however, it appears that nitrated carbon compounds have little or nothing to do with the imperfect precipitation, but that merely dissolving in nitric acid was not sufficient to form ortho-phosphate, in which state phosphorus must exist in order to be precipitated by ammonium molybdate. Evaporation to dryness and baking completes the oxidation of the phosphorus as well as destroys the carbon compounds, but the latter is merely incidental and not necessary.

Demands for a more rapid procedure led to a demonstration of the complete oxidation to ortho-phosphate in the wet way. The oxidizers most used are chromic acid and permanganate. The former is the less effective oxidant; it is not effective enough, in fact, in many cases, and it shows a tendency to soil the phospho-molybdate with chromic oxide. The latter, not counting the solitary exception recorded that it

does not act so completely with chilled iron as evaporation does, is quite efficient. After boiling for some time the excess of permanganate is destroyed by ferrous sulphate, oxalic acid, sulphurous acid, hydrogen peroxide, sugar, tartaric acid, potassium nitrite, hydrochloric acid, or other reducing agent.

If the phospho-molybdate has to be weighed, the behaviour of the silica, supposing it to be not eliminated by evaporation, is worth considering. Attention has already been drawn to the fact that when steel is dissolved in dilute (1.135 S. G.) nitric acid all the silica passes into solution and cannot be reprecipitated as silico-molybdate so long as the solution is kept acid. Ammonium nitrate, however, which is added to or formed in the solution in order to promote the precipitation of phospho-molybdate is said also to favour the formation of silico-molybdate.

*Precipitating the Phosphorus.*—As the precipitation is made in such diverse ways that it may be completed in five minutes or it may require five hours, it is obviously impossible to give an unqualified answer when asked whether ferric chloride, alkaline chloride, free hydrochloric acid, etc., may allowably be present. It depends entirely on how quickly the precipitation is required to complete itself and how little of the above substances and how much of others favourable to the precipitation are present. The complete precipitation of phosphorus is delayed by hydrofluoric acid for instance, but it is quite correct to say that it may be made in the presence of small amounts, although large amounts prevent it altogether. At these points the inexperienced go astray, but no information about them is so satisfactory as that obtained by personal observation and experiment. The most complete investigation we know of the formation of phospho-molybdate is that of Hundeshagen. A thorough experimental study of his paper is a most desirable piece of work for a student to do. A synopsis of the paper is given in Part xiii.

Like the ammonium magnesium phosphate, and most other precipitates, the formation of the dodeca-molybdate is hastened by shaking or forcibly passing air or gas through the solution, so that, except for special reasons, this operation need never take more than half an hour. There are several respected analysts, however, who contend that in order to obtain a definitely constituted compound free from iron, aluminium, manganese, etc., the solution should be allowed to cool before filtering off the precipitate. Others for a like reason form the precipitate in the cold, or recommend that it be redissolved and again precipitated under more precise conditions than were obtainable

in the first case. Both these complications are generally ignored in practice and the results are hardly less accurate than those obtained by the more elaborate operation.

Nitric acid and ammonium nitrate are more favourable to the precipitation of the phosphorus than any other acid and salt. They can be entirely replaced, not advantageously however, by sulphuric acid and sulphates. Ordinary steels are completely dissolved by nitric acid alone, and then the complete oxidation to ortho-phosphate with permanganate and the precipitation are but the work of a few minutes. Indeed by very vigorous shaking the precipitation is said to be complete in twenty seconds after the molybdate reagent has been added.

In the presence of arsenic an arsenio-molybdate is also precipitated—more or less. It forms less readily than the phospho-molybdate and is more easily dissociated by an excess of nitric acid, but, like the latter, it forms more readily in hot than in cold solutions. The amount of arsenic co-precipitated depends on the temperature at which the operation is performed and the time elapsing before the precipitate is filtered off. In a lengthy precipitation at 30° or 40° C., or in a shorter precipitation with shaking at 70°-80° C., very little arsenic comes down. Arsenic may be removed prior to the precipitation of the phosphorus by

- (1) Volatilizing with hydrochloric acid solutions of ferrous chloride, or, what is the same thing, evaporating the ferric solution with acid and a reducing agent.
- (2) By evolving as arsenuretted hydrogen with zinc from an acid solution.
- (3) Precipitation with sulphuretted hydrogen or an easily decomposable (zinc) sulphide in a handy form for subsequent estimation.

*Gravimetric Estimation of Phospho-molybdate.*—The precipitate, according to the more recent and reliable analyses, is ammonium phosphododeca-molybdate  $[(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3]$  when dried at 120° to 130° C. The earlier analyses are in some cases not trustworthy, because the conditions favourable to the formation of a definite compound were not well understood, and perhaps also because means of making a correct analysis were not well known. In order to make a direct weighing of the precipitate resource is had to

- (1) brushing from the dried filter paper,
- (2) using counterpoised filters, and
- (3) washing into a tared vessel and drying.

The drying in (1) and (2) is facilitated if the final washing is made with

alcohol, but the devices are subject to such obvious errors as the incomplete separation of the precipitate and paper, or the possibility of the balanced papers taking up unequal amounts of hygroscopic water. The darkening of the paper, which is sometimes referred to as an indication that the precipitate has been sufficiently dried, is also an indication that the phospho-molybdate has been reduced or has lost some of its ammonia. The third device is so troublesome that for works' purposes the first or second means are more extensively adopted, notwithstanding the above-mentioned objections.

A means of estimating the phospho-molybdate, which originated probably in a desire to avoid the tedious evaporation in a tared vessel, is to wash the precipitate into a specific gravity bottle, and from the known specific gravity of the substance to determine its weight. The required formula is

$$x = \frac{S}{S - s}(G - g).$$

where  $S$  is the specific gravity of the phospho-molybdate (*i.e.* 3.252);  $s$  that of the solution in which the precipitate is weighed;  $G$  the weight of the apparatus containing the solution and precipitate;  $g$  the weight of the same apparatus filled with the solution only, and  $x$  the weight of the precipitate to be determined.

It is a regrettable fact that the phospho-molybdate cannot be ignited, in the ordinary way, without being decomposed. But this has not prevented attempts being made to ignite the precipitate "so carefully that only the paper should be destroyed"; this can be done, we are informed, without loss of weight. By arranging the temperature to fall between 400° and 500° C. Meinecke gets rid of the paper completely, but finds that the ammonia has gone also, and a residue corresponding to  $P_2O_5 \cdot 24MoO_3$  is left. Perhaps the simplest and safest way of burning at this regulated temperature is to support the crucible containing the precipitate within a larger one, and to heat the latter by a suitable flame, as is done when manganese, cobalt, etc., are prepared for weighing as anhydrous sulphates. The authors believe that the means described on p. 55 *et seq.* for converting phospho-molybdate into a form which can be ignited without decomposition is the most satisfactory solution of this problem.

The most important feature of the nitro-molybdate reagent is the regulation of its acidity with respect to the solution precipitated, so that a less proportion of acid than dissociates phospho-molybdate (see Hundeshagen) may be present. Neutral solutions of ammonium molybdate have been and may be used when other conditions are arranged to correspond.

It is desirable to have a solution prepared in such a manner that little or no deposit forms on standing. The yellow deposit is usually pure molybdic oxide; its formation is promoted by having unnecessary amounts of ammonium nitrate in the mixture, but it cannot be altogether prevented except by using organic acids. The presence of tartaric acid is said to prevent the phospho-molybdate carrying molybdic oxide down. Eggertz says it prevents the formation of the main precipitate, Juptner says as much as 60 grams per litre may be used, and Veitch says its use is permissible but not advantageous.

Other means of estimating phosphorus gravimetrically depend on weighing as a compound of uranium, bismuth, mercury, lead, iron, or cerium. All are much inferior for the present purpose to the method just considered.

*Volumetric Estimation of Phospho-molybdate.*—The volumetric estimation of small amounts of phosphorus is satisfactory only when it has been separated as phospho-molybdate. The most-used processes are of an indirect kind, and depend on the determination of the associated molybdic oxide. Reduction with zinc in an acid solution to the sesquioxide, and re-oxidation with standard permanganate to the trioxide, is the oldest of these methods. The reduced solution appears to be very easily oxidized, and must therefore be treated with permanganate out of contact with the air. When the excess of zinc is filtered off, or the reduced solution in any way exposed, a partial reduction, which has given rise to intermediate expressions, such as  $\text{Mo}_8\text{O}_{13}$ ,  $\text{Mo}_{12}\text{O}_{19}$ ,  $\text{Mo}_{24}\text{O}_{37}$ , and so on, takes place; and unless precautions are taken at this stage, it is an easy matter to get results differing by ten per cent. Before reducing, the precipitate should be washed with a solution of sulphate, and not the nitrate of ammonium or dilute nitric acid.

A more rapid means of estimating the phosphorus, which has arisen since the constitution of the phospho-molybdate became better understood, depends on saturating the precipitate with caustic alkali, free from carbonate, and titrating the excess with dilute acid. In this way, it is claimed, a result may be obtained in from ten to twenty minutes, counting from the time the drillings are weighed out. An interesting but by no means so convenient a process is based on the reverse operation, that is, adding nitric acid to a neutral phospho-molybdate solution, filtering off the precipitate, and titrating the excess of acid. The estimation of the ammonia in the ammonium phospho-molybdate by Nesslerising and otherwise has been suggested, but generally disregarded because the ratio of the ammonia to the phosphorus is apt to vary.



A number of other methods are suited more to those occasions where some rapid means must be had rather to gauge the percentage of phosphorus than to accurately estimate it. These depend on :

1. Comparing the turbidities formed when a solution of the steel is shaken with ammonium molybdate.
2. The colour formed when the dissolved phospho-molybdate is poured into an acid solution of stannous chloride or sodium thio-sulphate ; or the colour formed with ferro-cyanide.
3. The volume occupied by a precipitate when it is settled in a graduated taper tube by whirling in a centrifugal machine.

Each of these processes must be worked under such conditions as obtained when the standards were prepared or the apparatus calibrated.

Of less interest from a steel-works' point of view are various other volumetric processes which in most cases are useful for estimating large amounts of phosphorus only. They may be briefly tabulated :

1. Direct titration with a neutral solution of ammonium molybdate until a precipitate of phospho-molybdate is no longer formed.
2. Iodometric estimation of the associated molybdic oxide by distilling with potassic iodide and hydrochloric acid or with potassium bromate.
3. Titration of the molybdenum with lead acetate and tannin (see page 83) after eliminating phosphorus with magnesia.
4. Addition of silver nitrate, lead acetate, etc., and estimation of excess of added metal in the filtrate, or its amount in the precipitated phosphate.
5. Formation of ammonium magnesium phosphate and estimation of the excess of standard ammonia added, or of the ammonia in the precipitate.
6. Titration with uranium nitrate using ferro-cyanide or cochineal as indicator.
7. Titration with ferric oxychloride or iron alum solution, using gallic or salicylic acid as indicator.
8. Precipitation as ammonium manganese phosphate and estimating the manganese after transforming to dioxide.
9. Measuring the amount of soda required to transform the monosodic to the disodic phosphate, using methyl-orange and phenolphthalein as indicators.



## THE ESTIMATION OF PHOSPHORUS.

In some papers on the analysis of molybdenum compounds, one of the authors showed that if to a solution containing molybdenum and phosphorus enough hydrochloric acid is added to prevent a precipitate from forming on adding at least enough lead acetate to combine with the molybdic and phosphoric oxides, and then this heated mixture is added to another containing ammonium chloride, and at least enough ammonium acetate to decompose the free hydrochloric acid, we get lead molybdate precipitated and an acid lead phosphate held in solution. The advantage of transforming the phospho-molybdate to lead molybdate in this way is that the latter is a perfectly definite and easily manipulated compound which can be ignited speedily without decomposition. Moreover, it weighs over one hundred and forty times heavier than the phosphorus that is being estimated.

Dissolve two grams of steel in 45 c.c. 1.20 nitric acid, and when the brown fumes are expelled, add permanganate until a pink colour or a precipitate of manganese dioxide persists on boiling. Clear the solution with ferrous ammonium sulphate or sulphurous acid, add 6 or 7 c.c. strong ammonia, and then to the clear hot solution 30 c.c. of the nitro-molybdate reagent. Shake the stoppered flask until the precipitate forms, and allow to stand from five to twenty minutes at 70-80° C.; when the precipitate has settled out leaving the solution clear, all the phosphorus is thrown down. Pass the solution through a pulp filter, wash with two per cent. nitric acid, dissolve the precipitate on the filter with a few drops of ammonia, wash with hot water, pass the solution again through the filter into a small beaker (200 c.c.) and wash. Add 10 to 12 c.c. concentrated hydrochloric acid, 10 c.c. lead acetate solution (40 grams per litre) and heat. In the washed-out flask heat a mixture of 50 c.c. ammonium chloride (200 grams per litre), and 50 c.c. strong ammonium acetate; mix the two solutions in the flask with shaking, filter, wash with hot water, and weigh the ignited lead molybdate. Its weight multiplied by 0.007<sup>1</sup> gives the weight of phosphorus in the steel.

Although it is desirable to work the process under the above described conditions, some variation in the amount of the free nitric acid, for instance, is allowable without sacrificing accuracy. Two separate steels were prepared as above, treated with varying amounts

<sup>1</sup> This factor is deduced from the relation between  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$  and  $\text{PbMoO}_4$ .

of strong ammonia after oxidizing with permanganate, and then finished as usual. The results were :

Ammonia Added.	Per cent. Phosphorus.	
	I.	II.
2 c.c.	0·088	0·032
4	·090	·032
6	·090	·034
8	·089	·034
10	·091	—

This process may be used for estimating phosphorus in pig irons, nickel steels and alloys, chrome steels, tungsten steels, spiegels, and ferro-manganeses. Chrome steels require more permanganate, as the chromium has to be oxidized to chromic acid; it must later be deoxidized by the sulphurous acid. Spiegels, ferro-manganese, and tungsten steels also require larger amounts of permanganate. If a little tungstic oxide is precipitated during the oxidation it should be removed before adding the molybdate. A little is sometimes precipitated with the phosphorus and gets weighed finally as lead tungstate; but in extreme cases only as much as influences the result by about 0·003 per cent. phosphorus has been found. The presence of tungsten in the lead molybdate is detected by dissolving in a small quantity of hydrochloric acid, evaporating nearly to dryness, and taking up with dilute hydrochloric acid. Any tungstic oxide remains undissolved, and may be allowed for by deducting its equivalent lead tungstate from the weighed lead molybdate. Further modifications required by the presence of special elements will be found where the analysis of such alloys is being considered.

Steels containing two to three per cent. chromium will frequently not dissolve completely in the nitric acid, even when digested with permanganate. On adding 5 c.c. dilute (1 to 3) sulphuric acid the action recommences after a few seconds with a slight explosion, and is quickly ended; in such cases an additional 2 or 3 c.c. ammonia should be added before precipitating the phosphorus. The addition of a little hydrofluoric acid also clears up the insoluble portion. But sometimes the still simpler expedient of diluting the solution, which no longer attacks the insoluble residue, with about its own volume of hot water will cause everything to dissolve.

The nitro-molybdate solution is made by dissolving fifty grams of molybdenum trioxide in 35 c.c. strong ammonia diluted with three times

its volume of water and pouring into 625 c.c. 1.20 nitric acid. A little molybdic oxide separates on keeping. The reagent made according to any other formula will do so long as the free acid in the precipitated solution is suitably adjusted.

The above process is very accurate ; it cannot, however, claim to be very rapid in comparison with some mentioned in the summary. A single estimation to be trustworthy needs at least half an hour from the time the drillings are weighed out, but a series of estimations can be made in proportionately less time ; *e.g.* thirty estimations have been made in a working day of seven hours by an experienced operator. The ability, however, to deal with large numbers of assays in a systematic and intelligent way is a faculty possessed differently by different persons. It also depends very considerably on the peculiar fitness of the apparatus for the work. The excuse for the following particulars, if they should appear commonplace, is that the aforementioned speed cannot be attained except by attending to such details.

Flasks similar to those used in liberating the carbon (page 13) are a suitable kind to use throughout the operation. A smooth funnel three and a quarter inches in diameter allows all the precipitated solution to be poured on the filter at once. The flask is washed out twice, and then the filter washed twice more, each time allowing all the solution to run through. Using pulp, the filtration is very rapid, and the washing particularly effective : a wash-bottle having no jet on the delivery tube is used. The yellow precipitate is conveniently dissolved by strong ammonia dropped from a burette. If the mixture of ammonium chloride and acetate is kept hot and the filter washed with hot water, the final precipitation can be made without further heating. When all the samples are precipitated as lead molybdate, the filtration and washing are carried out as before. On each occasion only so many filters are used as keep the time fully occupied ; more than this invites confusion. The filters are transferred to marked crucibles and placed six or eight at a time into the hot muffle ; under this severe treatment the precipitate never spatters.

It need hardly be remarked that to go through these operations thirty times a day is such a task as cannot be regularly discharged, even by the physically strong, except in a mechanical routine way. If the object of the assay is merely to detect abnormal amounts of phosphorus, the operation need not be carried, in the majority of cases, beyond the formation of the phospho-molybdate, as an experienced eye can gauge the percentage of phosphorus from the bulk of the precipitate with

tolerable accuracy. The toil of making a complete estimation may be lessened somewhat in the following manner, but the speed is not much increased, and it is easier for the final precipitate to contain accidental impurities. Dissolve the phospho-molybdate in ammonia as before, and pour the solution and washings into 50 c.c. of an acetic acid solution of lead acetate.<sup>1</sup> On the assumption that all the phosphorus is precipitated as lead phosphate, the composition of the white precipitate would correspond to  $\text{Pb}_3(\text{PO}_4)_2 \cdot 24\text{PbMoO}_4$ , which contains 0.644 per cent. phosphorus. But although only a portion of the phosphorus is precipitated under the above conditions, the deficiency introduces no appreciable error; in fact, the separate authors regularly use the two forms of the process respectively, and obtain results in perfect agreement. The precipitate may be ignited with the same freedom as before.

## CHROMIUM.

### PRELIMINARY SUMMARY.

**Separation of Iron and Chromium.**—To separate chromium from iron as a salt of the sesqui-oxide, the iron must be in the ferrous condition. The chromium may then be precipitated by adding barium carbonate, magnesia, zinc oxide, or sodium phosphate. The separation with barium carbonate to be complete requires the filtrate to be re-treated, so that at best the operation is a troublesome one and very little practised in spite of its frequent inclusion in text books. Chromic oxide may also be precipitated from iron solutions with nitroso- $\beta$ -naphthol or phenyl-hydrazine. Chromic and ferric oxides may be separated in the dry way by volatilizing the latter in a stream of hydrochloric acid gas at 200-300° C.; or the ignited oxides may be digested with hydrochloric acid and the insoluble chromic oxide filtered off. The treatment of the metallic borings with a neutral solution of cuprammonium chloride in a carbon dioxide atmosphere leaves all the chromium as a double carbide with iron; a further separation of the residual iron has therefore to be made (mainly by fusion) before the chromium can be estimated.

Those separations wherein the iron is eliminated after converting the chromium to chromic acid are very convenient. Hillebrand has

<sup>1</sup> Lead acetate crystals, 8 grams, and B.P. acetic acid, 400 c.c., made up to a litre with water.

observed that the characteristic green colour formed on fusing a salt of manganese with sodium carbonate may fail to appear when manganese is certainly present. We have observed that the formation of chromic acid when mixtures of ferric and chromic oxides are fused with sodium carbonate may also fail occasionally, and that the complete separation of the two oxides in this way may fail frequently.

The separation of iron from chromic acid solutions is a misunderstood process. An excess of alkaline acetate, ammonia, carbonate or bi-carbonate of sodium invariably precipitates part of the chromic acid with the iron, unless the amount of the latter is small or the excess of reagent large. An early and widely-published mode of making the separation is to oxidize the chromic oxide solution with bromine or chlorine, and to precipitate the iron with acetate. This operation may leave only a mere fraction of the chromic acid in solution; it is one of the most noticeable instances, unfortunately too common in analytical chemistry, of a serious misconception passing muster for many years in the best text books, which might have been corrected by a simple experiment on a synthetic mixture.

All separations of iron from chromic acid by means of alkalis or alkaline salts are subject to error through the formation of basic ferric chromates. The tendency of this compound to form is so decided that alkaline chromates may (in some cases with advantage) be used instead of acetates, sulphates, phosphates, etc., for precipitating neutralized ferric solutions when manganese, nickel, cobalt, zinc, or copper has to be estimated in the filtrate. For the same reason as obtains in the separation of iron and molybdenum, it is always best to make the separation by pouring the mixture *into* the caustic alkali or alkaline carbonate used to precipitate the iron. The following results obtained by adding alkali of binormal strength to a mixture of ferric chloride (equal to one gram of iron) and 30 c.c. of potassium chromate (12·5 grams per litre), illustrate the efficiency of some common reagents. Sodium hydrate is obviously the best.

Alkali in Excess.	Percentage Separation.		
	(NH <sub>4</sub> )HO.	Na <sub>2</sub> CO <sub>3</sub> .	NaHO.
0 c.c.	24·8	54·6	69·3
10	70·4	90·4	100·0
20	77·0	97·5	99·8
30	83·6	98·7	100·1
50	87·8	100·1	—

**The Gravimetric Estimation** of Chromium is generally made by adding ammonia, collecting the precipitated hydrate, and igniting it to chromic oxide. The precipitated hydrate is rather troublesome to wash, but it is improved in that respect if the precipitation is made in the presence of hydroxylamine. The precipitate also retains fixed alkalis, sulphuric and phosphoric acids, magnesia and other impurities, if they are in solution; and therefore the estimation in this form is limited almost entirely to pure solutions of chromic salts. By precipitating as phosphate, or basic phosphate ( $3\text{Cr}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5$ ), a purer precipitate is assured. Chromic oxide may also be precipitated as basic sulphite, and, if pure, ignited directly and weighed.

To make chromium the acid of the weighed compound it may be precipitated with a solution of a lead, barium, or mercurous salt. The use of either of the two first reagents is not interfered with by the presence of calcium, magnesium, zinc, nickel, cobalt, or manganese. Mercurous nitrate cannot, of course, be used satisfactorily if ammonium salts are present.

**The Volumetric Estimation** almost invariably requires the chromium to exist as chromic acid. The following reagents have been recommended for effecting the oxidation in the dry way :

Sodium carbonate alone or mixed with  $\text{KNO}_3$ ,  $\text{KClO}_3$ ,  $\text{K}_2\text{CO}_3 + \text{KClO}_3$ ,  $\text{KClO}_3 + \text{MgO}$ ,  $\text{K}_2\text{CO}_3 + \text{MgO}$ ,  $\text{K}_2\text{CO}_3 + \text{borax glass}$ ,  $\text{CaO}$ ,  $\text{CaCO}_3$ ,  $\text{BaO}_2$ ,  $\text{NaHO} + \text{CaO}$ ,  $\text{NaHO} + \text{MgO}$ .

Potassium carbonate, mixed with nitrate or caustic soda.

Caustic soda, mixed with lime or magnesia.

Caustic potash alone, or mixed with nitrate, or placed in an electric circuit.

Potassium nitrate.

Sodium peroxide, alone or mixed with barium peroxide.

Calcium chloride mixed with lime.

Soda lime, and potassium chlorate.

The following have been suggested for oxidizing the chromic oxide in the wet way :—Nitric acid and potassium chlorate, permanganate, manganese dioxide, lead peroxide, bromine, chlorine, iodine, mercuric oxide, hydrogen peroxide, sodium peroxide, and hypochlorites.

The list presents as great a variety, for working in either acid or alkaline liquids, as the analyst is likely to need.

Having converted the chromium to chromic acid, and separated from iron or not as occasion demands, it may be estimated, and most commonly is, by ferrous sulphate and permanganate or bichromate. But

stannous chloride, potassium iodide and thiosulphate, thiosulphate alone using iodide and starch as spot indicator, or iodine and arsenious oxide in bicarbonate or strong acetate solutions, have also been suggested. Some less used and apparently less convenient means of estimating chromic acid are :

1. Addition of baryta water, removal of excess with carbon dioxide, and titration of the free alkali, which is equivalent to the precipitated chromic acid.
2. Direct precipitation with barium chloride, using haematoxylin or logwood as indicator.
3. Processes depending on the addition of a reagent (*e.g.* a lead salt) which precipitates chromic acid, the excess used being estimated.
4. Two gasometric processes depending on the liberation of nitrogen on adding acidified hydrazine sulphate, or of oxygen on adding hydrogen peroxide, the evolved gases being measured at N.T.P.

The only noteworthy method for titrating solutions of chromic oxide is operated by running the solution into hot alkaline standard permanganate until a clear yellow colour is observed.

### ESTIMATION OF CHROMIUM.

Chromium is more easily and quickly, and for everyday purposes more accurately, estimated by a volumetric than a gravimetric process. Oxidation with permanganate in an acid solution, and titration of the chromic acid with ferrous sulphate, has been shown by experience to be a suitable form of process for estimating chromium in steel.

Chromium steels (but not ferro-chromium alloys) are decomposed by boiling with dilute sulphuric acid, and all the chromium goes into solution except what is associated with the black particles seen floating in the liquid. The addition of permanganate up to a certain point oxidizes the iron only according to the equation



When this reaction is completed the further addition of permanganate oxidizes the chromic oxide to chromic acid. But before this oxidation is really completed the excess of permanganate and the manganous sulphate in solution are mutually decomposed (see page 28) with formation of peroxide of manganese, and it is this precipitate that completes the oxidation in the boiling solution.



The speed of oxidation depends on the temperature, the excess of permanganate or manganese dioxide and the acidity of the solution. The change can be wrought with only a few drops of permanganate, (25 grams per litre), in excess of that theoretically needed, by boiling long enough; but with an excess of several cubic centimetres permanganate the oxidation is completed by a few minutes boiling. Increased acidity favours the oxidation; but this advantage is limited by the fact that, in strong sulphuric acid solutions, the peroxide of manganese may be partly dissolved without being completely decomposed, and is thus able to augment the measured oxidizing effect of the chromic acid. Moreover, in still stronger acid solutions, the complete conversion to chromic acid is impossible.

When the acid permanganate process was introduced the power of the precipitated dioxide of manganese to speedily and completely oxidize the chromium appears to have been overlooked; and it was customary to add permanganate to the boiling solution until its pink colour showed that free permanganic acid was present. This misconception led to a great deal of trouble, because no permanent pink colour is obtainable until all the manganous sulphate, which is formed by oxidizing the iron, is transformed to the dioxide, and this entails a big precipitate which invariably retains chromic acid.

The precipitated manganese dioxide was responsible, according to its amount, for a deficiency in each assay of from two to twenty per cent. In 1893 Mr. Galbraith proposed to free the precipitate from chromic acid by adding an excess of sodium hydrate and titrating the filtered alkaline chromate. A serious objection to this proposal is that unless all the manganous sulphate has been precipitated by permanganate, the added soda forms manganous hydrate, which, being a strong reducing agent, destroys a portion of the chromic acid, and may thus introduce a negative error many times greater than the one it was designed to avoid. On the other hand, if more permanganate than is required by the manganous sulphate is added, some additional device for destroying the excess is necessary in order to prevent permanganic being estimated as chromic acid. Galbraith's is perhaps the least happy modification of his original process, but it brings out a useful fact, viz.: that chromic acid associated with manganese dioxide can be easily separated by treatment with caustic soda.

#### **Stead's Modification.**

Mr. Stead showed that the black chromiferous particles seen in the sulphuric acid solution of the steel are decomposed during the perman-



ganate oxidation. His modified process is based on the fact that a dilute solution of hydrochloric acid will destroy manganese dioxide or permanganate without in the least decomposing chromic acid.

Dissolve two grams of steel in 30 c.c. dilute sulphuric acid (1 to 3), oxidize the iron with permanganate, dilute to 300 c.c. with water, and add half a gram of permanganate crystals dissolved in water. After boiling for ten minutes add 40 c.c. strong hydrochloric acid diluted with 40 c.c. hot water, and continue the boiling until the brown peroxide has just disappeared; then add 150 c.c. boiling water, and continue the boiling until 100 c.c. has evaporated: the solution is then free from chlorine, and after cooling ready to be titrated with ferrous sulphate and bichromate.

This process does not enable one to judge by the colour of the titrated solution what amount of chromium is likely to be present, as it is sometimes desirable to do. The process would also be more speedy and none the less accurate if a smaller excess of permanganate were added after the iron has been oxidized. This would also help to minimize the possibility of error through the formation of manganous ferro-cyanide and a premature end reaction. Iodized starch paper may be used to indicate the expulsion of chlorine from the boiling solution.

#### **Another Modification (after Vignal).**

To two grams of steel add 20 c.c. dilute sulphuric acid (1 to 3), and boil until the sample is at least mainly dissolved, then add 20 c.c. 1:20 nitric acid, boil to complete the oxidation of the iron, and dilute to about 200 c.c. It is unnecessary to have more than 2 c.c. permanganate (25 grams per litre) present over and above that used in converting the chromium to chromic acid, and therefore, after adding permanganate until a turbidity persists, add only another 2 c.c.

When the sample is dissolved in this way chromic oxide is the only oxidizable body in solution, so that if dilute permanganate were run in from a burette until a faint turbidity of manganese dioxide was formed, the amount used would measure the approximate percentage of chromium present; indeed, this information is obtained very roughly by using the stronger permanganate.

After five or ten minutes' boiling the excess of permanganate may have been converted to manganese dioxide; if this is not so, then add a little manganous sulphate and continue the boiling. Filter through asbestos. When the washings are no longer yellow, pour on to the filter 10-20 c.c. hot sodium hydrate of binormal strength, catch the filtrate in dilute sulphuric acid, and if there is any colour

add to the (meanwhile cooled) main filtrate, and titrate with ferrous ammonium sulphate and permanganate. The sodium hydrate, it has been found, recovers from .01 to .03 per cent. of chromium from the precipitate.

The calculation is the same as for bichromate solutions: that is, the iron value of the standard solution multiplied by 0.311 equals the chromium value; or for solutions exactly decinormal, 1 c.c. = .001736 grams chromium; or when two grams of steel are used,

$$1 \text{ c.c. } \frac{N}{10} \text{ KMnO}_4 = .0868 \text{ per cent. chromium.}$$

The use of nitric acid avoids the introduction of so large an amount of manganese as when the sulphuric acid iron solution is oxidized with permanganate; this also makes it impossible to form a large precipitate of peroxide before a permanent pink is shown. Moreover, the presence of nitric acid causes the precipitate to be much more easily filtered, and the single washing with caustic soda frees it entirely from chromic acid.

If two grams of steel containing no chromium are assayed in the above manner, a consumption of ferrous sulphate equivalent to about 0.08 per cent. chromium will be observed. This amount must therefore be deducted from each result in order to arrive at the true percentage; or the caustic soda washing may be omitted and 0.05 per cent. deducted. A determination of chromium by this latter process can be made in twenty minutes or less.

## NICKEL.

### PRELIMINARY SUMMARY.

**Separating the Iron.**—The better-known and most-used processes for the separation of iron from nickel are the same in principle as those used for separating iron and manganese (page 25), but generally the former operation must be much more delicately made in order to ensure a perfect separation. The acetate separation, which is as convenient and certainly as accurate when properly performed as any known process, is explained at some length on page 67 *et seq.*

The separation of iron and nickel with ammonia is a process of which much that is unintelligible can be gathered by turning from one authority to another. This confusion is due, no doubt, to differences

in modes of working, whose true significance is either not appreciated or not well understood. The differences briefly catalogued are :

1. The use of various acid solutions.
2. Precipitation in hot or cold solutions.
3. The rate at which the precipitation is made.
4. The presence of various ammoniacal salts: chloride, sulphate, oxalate, borate, etc.
5. The excess of ammonia used.
6. The time allowed for the solution to digest.

All these particulars may not have a material influence on the result, but if an excess of ammonia is used then due regard *must be* paid to 4 if an accurate separation is desired.

The futility of making an accurate separation, when the amount of iron to be precipitated is very large, merely by adding ammonia to an acid solution of the two metals is a matter of common experience. In order to make amends, hydrochloric acid, so dilute as barely to attack the precipitated ferric hydrate, is added to the ammoniacal solution; this redissolves the nickel which has been carried down, and the small amount of iron which accompanies it is removed or not according to the influence it may exert on the subsequent estimation.

Of the reagents mentioned on page 26, alkaline sulphates and phosphates are the most widely used for separating iron and nickel; but many of the others have features which specially fit them for particular uses, *e.g.* chromates in great excess may be added to the neutralized ferric solution without the smallest fraction of the nickel being precipitated with the iron. Eastwick's process, frequently referred to by American chemists, depends on the solubility of the sulphide of nickel and the insolubility of the sulphide of iron in an acid solution of ammonium sulphate; Rosenblatt's, on the precipitation of the iron with potassium thio-carbonate; and others, on the diverse solubility of the sulphides in hydrochloric acid, or of the hydrochloric acid solution of the salts in ether. Some of these are general processes which sharply separate iron, aluminium, chromium, etc., from nickel, cobalt, manganese, copper, zinc, etc.

Iron may be electro-deposited from alkaline tartrate solutions free from nickel. But generally the electrolytic separation is made in alkaline solutions in which the precipitated iron is suspended; or, the nickel and iron are deposited together in an ammoniacal solution containing an organic (citric) acid, and then on reversing the current, in an ammoniacal solution of ammonium sulphate, the nickel is redeposited

and the iron floats as precipitated hydrate. Chromic acid prevents the electro-deposition of nickel.

When the separation is effected by precipitating the nickel, the iron is held in solution as pyrophosphate, or by being transformed into ferro-cyanide and the nickel precipitated with bromine and soda or sodium xanthate. The only other noteworthy operations of this class depend on the diverse solubility of the oxalates of nickel and iron in dilute acetic acid.

**Gravimetric Estimation.**—The mode of separating the iron occasionally proscribes a certain form of estimation, but the precipitation of the nickel as sulphide is of very general application, *e.g.* it can be used in the presence of many organic salts and the acids of sulphur and phosphorus. The completeness of the precipitation depends on the ratio of the weight of acid to the weight of metal in solution, and by suitable adjustment of this proportion a number of separations from nickel can be made. In inexperienced hands the precipitation is frequently found to be incomplete, the deficiency being due, it is said, to the formation of a thio-nickelate. According to Gibbs, nickel may be completely precipitated by a small excess of sodium carbonate, but generally, when ammonia salts are absent, the precipitation as nickelic hydrate with bromine and soda is more convenient. Both sulphide and hydrate must be converted before weighing either to the oxide or the sulphate. The latter has several times been recommended as the best form in which to weigh the nickel. Clark has described a process in which the nickel is precipitated with ammonium phosphate and weighed as pyrophosphate; cobalt, if present as peroxide, does not interfere.

On very rare occasions the ignited oxide is reduced to the metal in a current of hydrogen. But generally when nickel is weighed in the metallic state it has been electro-deposited. This is the only operation in electro-analysis which can be commonly met with in the steel-works laboratory, and this even is inferior in point of convenience, and by no means superior in point of accuracy to the cyanometric estimation.<sup>1</sup> The deposition is made from solutions of the chloride, sulphate, pyro-

<sup>1</sup> Electrolytic determinations and separations are always interesting and at times are indispensable. They seem generally, however, to be very much overrated. For example, in his Presidential Address to the Society of Chemical Industry, J. W. Swan, F.R.S., is reported to have said that "Copper, nickel, cobalt, lead, antimony, and bismuth are more quickly and conveniently determined by electrolytic than by the ordinary gravimetric or volumetric methods of analysis." So far as copper, nickel, lead, and antimony are concerned this seems to us an exaggerated statement.

phosphate, or oxalate. Manganese, if present, contaminates the precipitated metal.

**The Volumetric Estimation** depending on the precipitation of the nickel as a higher oxide, and its titration with various reducing agents, is by no means unanimously approved of. The contradictions refer mainly to the exact state of oxidation of the compound. Respected names could be arranged on either side, and therefore one's belief should rest rather on personal investigation than on authority. Much of the confusion is undoubtedly due to the fact that the higher oxide is decomposed, perhaps at ordinary temperatures, but certainly in heated liquids. Nickel may be precipitated as oxalate and the excess of the reagent or the washed precipitate titrated with permanganate after the fashion of the volumetric estimation of lime. It may also be titrated with sodium sulphide, using the nitro-prusside indicator, even in the presence of copper. There are also processes depending on comparison of the colour formed in solutions of nickel salts by ammonia and by potassium sulpho-carbonate.

The cyanometric estimation is one of the most stable and exact processes to be found in the literature of metallurgical analysis. Déniges showed that any silver salt, or any compound which modified a silver salt in a regular fashion, could be estimated by means of potassium cyanide, using a precipitate of silver iodide formed in the solution as indicator. Before Déniges' paper appeared a cyanometric estimation of nickel had been used, in which the changed colour of cupric ferro-cyanide when potassium cyanide is added acted as indicator; but it was neither so sensitive nor so free from disturbance under varying conditions as is the precipitated silver iodide. The process is described on page 71. Moore is said to have first applied silver iodide to detect the point at which the double cyanide of nickel and potassium is formed.

## THE ESTIMATION OF NICKEL.

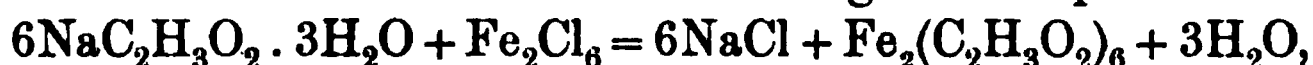
### Separating the Iron as Basic Acetate.

The word 'neutralized,' when applied to the ferric solution to which the acetate is added, has a special meaning which necessitates explanation. On adding ammonia (or any other alkali or alkaline carbonate) to an acid solution of ferric chloride all the free acid is first destroyed. Afterwards the ferric hydrate precipitated by repeated additions of small amounts of ammonia is dissolved,

at first easily, in the ferric chloride, and the clear yellow solution becomes red. This operation goes on most quickly when a carbonated alkali is used, because the liberated carbon dioxide aerates the flocks of ferric hydrate and makes them easy to dissolve. But whatever alkali is used a point is reached beyond which, if a precipitate be formed, it is not redissolved, however long the solution may stand, that is to say, the undecomposed ferric chloride becomes saturated with ferric hydrate. The solution has now a deep red colour, and may be represented approximately by  $\text{Fe}_2\text{Cl}_6 \cdot 8\text{Fe}_2(\text{HO})_6$ , or if solutions of ferric nitrate are operated on nine and a half times as much iron may exist as  $\text{Fe}_2(\text{HO})_6$  as there is in the  $\text{Fe}_2(\text{NO}_3)_6$  which keeps it dissolved.

Dilute solutions of ferric chloride are decomposed and become turbid on heating. In the same way, when 'neutralized' solutions are diluted and heated, the eight or nine molecules of ferric hydrate are precipitated, because the one molecule of ferric chloride in which they were dissolved is decomposed; so that by heating a dilute solution of ferric chloride, saturated with its own hydrate, all the iron may be precipitated without the assistance of acetates, sulphates, or phosphates, but it requires both patience and skill to do this effectively and repeatedly with all kinds of ferric solutions.

A solution of ferric chloride containing no free acid and no ferric hydrate reacts with sodium acetate according to the equation



whence it follows that eight grams of crystallized sodium acetate are needed to precipitate one gram of metallic iron. In neutralized solutions acetate is needed only to precipitate that portion of the iron not already precipitated as hydrate; that is to say, considerably less than one gram of sodium acetate will be needed to precipitate one gram of iron even if we take no account of the spontaneous decomposition of heated and diluted solutions of ferric chloride.

Solutions of ferric acetate are decomposed on heating; the precise temperature at which this takes place depends to some extent on the presence of alkaline salts, such as chlorides and nitrates, but mainly on the amount of alkaline acetate present over and above that necessary to transform all the ferric chloride into ferric acetate. The precipitated ferric acetate is not a very stable body; in boiling solutions it becomes converted into ferric oxide and free acetic acid, and therefore the composition of the precipitated basic acetate will depend, in the first instance, on the proportion of dissolved hydrate held in solution by undecomposed ferric chloride; and then, on the extent to which the

precipitated ferric hydrate and acetate are decomposed by heating. It must always have an indefinite composition such as may be represented by



The separation of iron (or aluminium) from nickel (cobalt, zinc, manganese, or copper), depends on the fact that solutions of ferric (or aluminic) acetate are decomposed at 100° C., while the acetates of nickel (Mn, Zn, Co, and Cu) are only decomposed at a considerably higher temperature (175° C.). In the presence of a large excess of alkaline acetate, however, the ferric compound is decomposable at ordinary temperatures, and in the same way, at any rate when iron is present also, the acetates of nickel, cobalt, etc., may be decomposed at boiling point, or below. On being precipitated the acetates of these latter metals become also transformed into the metallic oxide and free acetic acid, but they are very dissimilar in their tendencies to be precipitated with the iron. Manganese, for example, will not go down with the iron when twenty times the necessary amount of acetate is used; the order of stability of the rest is zinc, cobalt, nickel, copper; the perfect separation of the last-named element is hardly possible by a single precipitation of the iron as basic acetate.

Acetic acid should be added before the acetate, in order to minimize the danger of nickel going down with the iron. This is done because the oxides of all the metals, which it is desirable to keep in solution, are soluble in such an acidified liquid.

In the following table a summary of the behaviour of the various elements when separated with varying amounts of acetate is given. Each separation was made from a solution containing one gram of iron and one decigram of the respective metal. The solutions were completely neutralized, and each contained 10 c.c. of acetic acid. In some cases sodium acetate was used, in others ammonium acetate. This is the only difference in the treatment of the respective elements, and does not, we believe, involve a change in the percentage recovery large enough to give any element precedence of its neighbour.

Dilute Acetate Used.	Percentage Separation from Iron of				
	Mn.	Zn.	Co.	Ni.	Cu.
10 c.c.	100·0	—	100·0	100·0	98·0
20	100·0	100·8	99·0	99·0	92·9
50	100·0	97·6	97·5	95·2	69·6
100	100·0	—	93·8	90·0	53·1



It has been repeatedly recommended that the acetate should be added to the cold solution, and the mixture then raised to boiling. This procedure is supposed in some degree to compensate for the addition of any injurious excess of acetate. This is, however, not merely a useless and troublesome, but actually a harmful recommendation. The mischief is apparent if we consider the causes from which an imperfect separation may arise, viz.: the excess of alkaline acetate, and the ferric acetate in *the act of precipitating*. When acetate is added to the cold solution both these factors exert their maximum influence, but on adding it to the boiling solution the first portion completes the precipitation of the iron, and the remainder is added to a solution in which the iron is suspended merely. Thus by precipitating with a purposed excess of acetate at 16° C., only 83·3 per cent. of the nickel present remained in solution; at 60° 86·3 per cent., at 80° 91·0 per cent., and at boiling point 94·7 per cent. of the nickel was found in the filtrate. This difference is an important one to those who prefer to use reagents in "a free and easy" manner, for, on comparing the influence exerted by increasing amounts of acetate when added to the cold (I.) and boiling solutions (II.), the advantage is seen to be all against the generally accepted procedure; in fact, the acetate could not be added at a more unfavourable moment than when the solution is cold.

Dilute Acetate Used.	Percentage Nickel Recovered.	
	I.	II.
10	100·0	—
20	99·0	99·8
50	95·2	98·1
100	90·0	94·8

We hope the extended treatment of 'acetate separations' may gain for them the practical appreciation they deserve. Many highly esteemed reagents would lead to quite untrustworthy results if their peculiar properties were disregarded, as those of alkaline acetates have been.

**To Estimate Nickel** in steel dissolve two grams of the borings in hydrochloric acid, oxidize with nitric acid, and add ammonia until the colour, changing from yellow to red, shows that all free acid has been neutralized. If a solution of ammonium carbonate of known strength is available, so much of it can be added at once as will nearly form  $\text{Fe}_2\text{Cl}_6, 8\text{Fe}_2(\text{HO})_6$ : otherwise the complete neutralization is made by



adding ammonium carbonate a few c.c. at a time in rapid succession to the whirled solution. It is unnecessary to wait for succeeding precipitates to disappear, because finally the addition of a few c.c. of the carbonate causes a precipitate altogether unlike any preceding one: it is thicker and pulls irregularly on the hand as the flask is whirled. When the volume of solution is not large it is almost like a jelly. This unmistakably permanent precipitate can be produced in about a minute. On adding 10-15 c.c. acetic acid the turbidity quickly disappears, part of the acid going to form ammonium acetate; dilute then with hot water to nearly a litre, and heat to boiling. The iron should not be more than partly precipitated at this stage. Supposing no ammonium carbonate to have been added beyond what was necessary to neutralize the solution, then only twenty c.c. of dilute acetate<sup>1</sup> would be needed to precipitate all the iron; so that when the neutralization is made after the above fashion, always less than twenty c.c. is required. If the ammonium carbonate has been seriously over-added, and too large an excess of acetate formed, it betrays itself by the heated solution becoming turbid long before boiling point is reached. A turbidity forming below 75° C. is hardly consistent with a perfect separation, but the fault can be corrected by adding a suitable amount of hydrochloric acid. The precipitated solution may be made up to a litre and 500 c.c. filtered off; or, a portion of the supernatant solution being taken to make up a filter with dry asbestos on a perforated plate, 500 c.c. is poured through, and the rest, asbestos and all, measured.

#### **Cyanometric Determination of the Nickel.**

To the filtered solution add 2 c.c. sulphuric acid, or an equivalent amount of ammonium sulphate, neutralize, add 20 c.c. binormal ammonia (the precise excess of ammonia is not important, but there is a limit to its advantageous use), 2 c.c. of a 20 per cent. potassium iodide solution, and 5 c.c. silver nitrate (two grs. per litre). Run in a solution of potassium cyanide of such strength that about 70 c.c. is equivalent to a decigram of nickel. After enough has been added to form the double cyanide of nickel and potassium the silver iodide turbidity decreases, and finally clears up completely. Recall it by adding a few c.c. more silver nitrate, and then add the potassium cyanide carefully until one drop disperses the faint opalescence. From the potassium cyanide used deduct the amount which has been used

<sup>1</sup> 50 grams  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$  crystals per litre or 75 c.c. ammonium acetate, made by neutralizing 33 per cent. acetic acid with '880 ammonia, diluted to one litre.

by the added silver nitrate and calculate the remainder to grams nickel. The potassium cyanide is standardized with electro-deposited nickel or some reliable nickel compound (*e.g.* re-crystallized nickel ammonium sulphate) and the value of each c.c. deduced. Some further details of the use of this process are given in connection with the analysis of nickel alloys.

### The Separation of Iron and Nickel with Ammonia.

By pouring an excess of ammonia into an aqua regia solution of one gram of a ten per cent. ferro-nickel, or by pouring the alloy solution into the ammonia, the nickel in the filtrate may vary from three to thirty per cent. of the correct amount, according to the excess of ammonia used. The operation is a very easy one, but, in this form, it would need repeating many times in order to separate all the nickel.

The separation is not imperfect, as some others are, on account of some influence exerted by the iron at the *moment of its precipitation*; because if we precipitate ferric chloride with an excess of ammonia, add a solution of a nickel salt, shake, and filter, we find almost as little nickel in the filtrate as though the iron had been precipitated in its presence. The error arises through the adsorption of the ammoniacal nickel compound by the precipitated ferric hydrate, just as sand, filter paper, etc., will extract particular salts from their solutions, or from mixtures of salt solutions.

Ammoniacal chlorides, nitrates, sulphates, etc., have the power of checking the adsorption. They act by forming the double chloride, nitrate, or sulphate of nickel-ammonium, but very large amounts must be added in order to completely eliminate the error. The comparative value of such additions when one decigram of nickel was being separated from one gram of iron have been observed by neutralizing 50 c.c. .880 ammonia to the chloride, nitrate, and sulphate respectively, and precipitating each of the iron solutions containing one of these salts with an equal amount of ammonia. The nickel found in the solutions was

Ammon. Salt.	Grm. Ni. Recovered.
Chloride, - - -	0.0607
Nitrate, - - -	0.0584
Sulphate, - - -	0.0573
None, - - -	0.0083

The results may be improved by increasing the amounts of ammonium salts and ammonia until a perfect separation of the iron and nickel is obtained.

By substituting potassium cyanide for the ammonium salt a perfect separation can be effected when very little more is present than is needed to form the double cyanide of nickel-potassium  $[\text{Ni}(\text{CN})_2, 2\text{KCN}]$ . Thus the decigram of nickel mixed with the solution of one gram of iron would require 66.4 c.c. cyanide to form the double cyanide. With the varying amounts of cyanide shown below the nickel which remained in solution when the mixture was poured into an excess of ammonia was

C.c. KCN Used.	Grm. Ni. Recovered.
70	0.09991
100	0.09985
150	0.09994

In the above series the nickel was estimated cyanometrically after boiling the acidified solution so as to decompose the double cyanide. The cyanide is not a convenient solution from which to precipitate nickel electrolytically, but such as prefer gravimetric processes will find, if the iron be precipitated with caustic soda instead of ammonia, that the cyanides are readily decomposed and the nickel sesquioxide precipitated with bromine (and soda if necessary).

If potassium cyanide of known strength is used it is quite feasible to estimate the excess in an aliquot part of the filtrate by means of silver nitrate and potassium iodide. In that form the process is the most rapid available means of estimating nickel in ferro-alloys, which includes also a separation of the iron. With care to dissolve always in the same amount of acid, and to use other reagents of known strength, the operations may be concluded in the same time as is needed to make an Eggertz carbon test on the furnace stage, and as it is not interfered with by the presence of chromium it is well suited to the circumstances under which such tests are required.

Nickel is adsorbed by precipitated ferric hydrate to an appreciable extent from ammoniacal solutions only; in fact, on making the solution so faintly acid that the precipitated ferric hydrate is hardly at all dissolved the adsorbed nickel goes again into solution. With like reason, when the iron is precipitated, preferably after adding several grams ammonium chloride, with so little ammonia that finally the filtrate is distinctly acid, the separation is a good one. The Schwarzenberg separation,

which depends on the nice adjustment in the cold solution of the  $x\text{Fe}_2\text{Cl}_6 \cdot y\text{Fe}_2(\text{HO})_6$  compound, so that when the ammonia is no longer to be added, to use Fresenius' words, "the fluid fails to recover its clearness after standing some time, but on the contrary becomes rather more turbid than otherwise," is but a particular mode of performing this operation.

The least troublesome way of precipitating the iron with so little ammonia that the solution still remains distinctly acid is as follows: Heat the acid solution of the iron and nickel to boiling; at this temperature the ferric hydrate first precipitated is easily dissolved by the ferric chloride, and very little time is lost in obtaining a turbid solution, which, however, does not hold any filtrable precipitate, and is really obtained with less ammonia or ammonium carbonate than would be needed to form a lasting precipitate in the cold solution. From this point only a *very dilute* solution of ammonia should be used, and when the total ammonia added is equal to or somewhat less in amount than would have been needed to form a permanent precipitate if the 'neutralization' had been made in the cold solution, the iron will have been precipitated. The operation requires considerable care and attention, but is not otherwise a difficult one; its success depends entirely on keeping the solution acid throughout, for if the solution be ever so slightly alkaline the separation is imperfect.

Appended are examples of separations: made as above (II.); in the same way, but adding 2 or 3 c.c. acetic acid after precipitating (I. and IV.); as in II., but adding a few c.c. acetic acid before precipitating (III.). The process could be advantageously modified in various other ways.

	Present.		Found.
	Grms. Fe.	Grms. Ni.	Grms. Ni.
I.	1	0·20	0·1999
II.	1	·10	0·0998
III.	1	·05	0·0497
IV.	2	·10	0·1002
V.	2	·03	0·0298

**TUNGSTEN.**

## PRELIMINARY SUMMARY.

**Separation from Iron.**—Literature relating to the estimation of tungsten in steel is comparatively scarce, and most processes met with are modifications one of another. Iron and tungsten may be separated by fusion of their oxides with sodium carbonate, nitrate, or hydrate. This method of separation is seldom resorted to, because it is simpler and quite as accurate to effect a separation by precipitating the tungsten from a solution of the two metals in one or other of the following ways. The steel may be decomposed with nitric acid, aqua regia, nitro-sulphuric acid, brominized hydrochloric acid, or hydrochloric acid alone. When the last of these is used alone and air excluded, metallic tungsten is left undissolved, and very little passes into solution. With the other reagents it goes wholly into solution, or is partly precipitated as the trioxide. On evaporation to dryness, or to appearance of fumes of sulphur trioxide (according to the solvent used), the tungstic oxide, along with silica, separates out and does not dissolve again on dilution, or on treatment with sufficient dilute hydrochloric acid to hold the iron in solution. The same result is reached by decomposing the steel with cuprammonium chloride solution, and igniting the residue left after filtration. This is an easier process than the others mentioned, particularly as regards filtration, but it is interfered with by the presence of chromium, and this considerably limits its usefulness, in these days, when this metal is so frequently associated with tungsten in steel.

**Separation from Silica.**—In whatever way the tungsten is separated, it is invariably accompanied by silica when silicon is present, as it nearly always is, in the steel. It should now be a well-known fact that the separation of silica and tungstic oxide cannot be made with ammonia. Since Dufty drew attention to the errors which were introduced by the solubility of silica in ammonia solutions, there has been a general abandonment of the process, so that no further comment is necessary, except in so far as it offers an occasion to point out how an analytical error may be perpetuated, and even originated and accepted as truth, in spite of previously published evidence invalidating the principle on which its existence depends. As long ago as 1868 Skey and Pibram drew attention to the solubility of ignited silica in ammonia, and actually determined its solubility when treated

in various ways. One may be prejudiced in favour of certain methods by the "was grau vor Alter ist, das ist ihm gottlich" sentiment, but it ought not to deter one from verifying them, nor from rejecting them when found wanting.

The volatilization of the silica with hydrofluoric acid, with or without the addition of sulphuric acid, is now the commonly used means of separating silica and tungstic oxide; sometimes, however, fusion with hydrogen potassium sulphate, which leaves the silica after extraction; and volatilization as silicon tetrachloride in a current of chlorine, are resorted to.

**Gravimetric Estimation.**—When the tungsten is obtained as a soluble tungstate, or the tungstic oxide is converted to that state by a fusion, as it sometimes is without good reason, the precipitation may be made from the neutral or faintly acid liquid with mercurous nitrate, quinine acetate, lead acetate, or salts of barium and cadmium. The mercurous salt is suitable when pure solutions are being dealt with, and the lead salt is very convenient when a mixture of tungstate and molybdate has to be precipitated.

**Volumetric Estimation.**—There is no highly commendable volumetric process for the estimation of tungsten. Such as have been suggested are: (1) dissolve tungstic oxide in standard sodium hydrate, and titrate excess of alkali with standard acid; (2) precipitate with standard uranium solution, using the ferro-cyanide indicator; (3) add the reduced acid solution of a soluble tungstate to an excess of permanganate, and determine the excess with ferrous sulphate.

### THE ESTIMATION OF TUNGSTEN.

When tungsten is separated from iron by evaporating the nitric or nitro-hydrochloric solution and 'taking up' in hydrochloric acid, it is occasionally stated that the acid extract should be evaporated once or twice more in order to ensure the complete separation of the tungstic oxide, some of which, with only one or two evaporations, is liable to remain dissolved in the hydrochloric acid solution. These instructions are based on the very common assumption that the tungstic oxide separated by the first evaporation remains as a precipitate whilst the second evaporation is in progress; this, however, is by no means the case. Unless tungstic oxide has been ignited at redness it is very appreciably soluble in hydrochloric acid, so that after

repeated evaporations to any extent the final 'take-up' in concentrated acid always carries into solution much more oxide of tungsten than was supposed to be unprecipitated after the first evaporation, and this is only precipitated after evaporation to low bulk or by immediate dilution with water. As a matter of fact, tungstic oxide is hardly, if at all, soluble in hydrochloric acid which has been diluted with two or three times its own volume of water.

Any of the processes indicated in the preliminary summary, after the tungstic oxide has been purified from silica and traces of ferric oxide, and the tungsten calculated either by difference or estimated after fusion by precipitating the neutralized solution of the melt with mercurous nitrate, gives satisfactory results with carbon-tungsten steels; the extreme results of estimations made on the same steel in seven different ways were 4.32 and 4.46 per cent. tungsten.

#### **Rapid Acid Evaporation Process.**

The following process is not a perfectly accurate one, the results being generally about 0.05 per cent. low. It is, however, more rapid than any other form of the acid process, and either with or without the correction named is satisfactory for technical purposes. The course of the reactions is most clearly seen when the process is applied to a sample containing very little carbon.

Digest 5 grams of the borings with 50-100 c.c. concentrated hydrochloric acid just short of the boiling point. The iron is easily attacked, but the tungsten is not. On adding a few drops of concentrated nitric acid, the ferrous changes to ferric chloride, and then the tungsten is visibly acted upon until the clear orange-coloured ferric chloride blackens again, showing that some ferrous chloride has been reformed. By a repetition of the addition of nitric acid as required, but so as to demand a total consumption of that acid very slightly greater than would transform the iron wholly to the ferric condition, the sample passes completely into solution in a few minutes. This may seem to be contrary to the experience of those who have frequently decomposed tungsten steels and alloys with aqua regia, and have noticed that tungstic oxide, usually brown and impure, invariably separates; but the explanation is to be found in the use of sufficient hydrochloric acid to dissolve completely all the tungstic oxide, and of no more oxidant than is necessary for the oxidation. If now the acid solution of the metal be boiled until tungstic oxide *just begins* to separate, and then diluted with at least twice its volume of hot water and again boiled, all



the oxide is precipitated except two or three milligrams.<sup>1</sup> The ignited precipitate contains silica, which is removed with hydrofluoric acid; it also contains traces of ferric oxide, which may be allowed for by fusing with sodium carbonate, extracting with water, filtering off the ferric oxide, igniting and weighing.

The essential points of the process consist in the presence of sufficient hydrochloric acid to keep the tungstic oxide in solution until decomposition is complete, and in maintaining the strength of the acid during the decomposition. On the latter account the solution, although hot, is not allowed to boil. The smaller the excess of acid over necessary requirements, the greater the economy of material, and of time occupied in the subsequent evaporation.

After separating traces of ferric oxide from the sodium carbonate fusion, the aqueous filtrate may have a faint yellow colour due to sodium chromate. This may be allowed for by acidifying and titrating with ferrous sulphate and potassium permanganate; the amount of equivalent chromic oxide being deducted along with the weight of ferric oxide. From steels containing three per cent. of chromium we have never met with as much as one milligram of chromic oxide in the tungsten residue.

#### **Modified Schöffel Process.**

In 1879 Schöffel proposed to treat the steel borings with a neutral solution of sodium or ammonium copper chloride, such as was used for liberating carbon from iron, to ignite the carbonaceous residue, separate the silica, and precipitate the extract of an alkaline fusion of the tungstic oxide with mercurous nitrate.

Besides carbon, tungsten, and silicon, the residue, after decomposition of the steel with the double copper compound, contains sulphur as sulphide of manganese or iron, chromium associated with considerable amounts of iron, titanium (if present at all), and all the phosphorus if the copper solution used is quite neutral.

The small amounts of sulphur and phosphorus in the steel would not seriously affect the tungsten estimation if the result were arrived at by difference after ignition, elimination of the silica with hydrofluoric acid, fusion of the residue with sodium carbonate, and weighing of the small amounts of ferric oxide, etc., left after aqueous extraction. Such a procedure, in fact, gives very accurate results with pure carbon-

<sup>1</sup> When the diluted solution has, for some reason or other, been allowed to stand for some time in a warm place, we have been unable to detect any  $\text{WO}_3$  by evaporating the filtrate.



tungsten steels, but when chromium is present the amount of iron oxide to be filtered off after the sodium carbonate fusion may be comparatively large, and considerable amounts of chromium pass into solution along with the tungsten when the melt is extracted with water.

It may occasionally happen that the tungstic oxide obtained by difference in the above manner from a chrome-tungsten steel is less than the amount of impurities associated with it, and herein lies the weakness of Schöffel's process for general purposes.

By decomposing chrome-tungsten steels with copper solutions which contain an increasing amount of hydrochloric acid, the amount of impurity to be found in the ignited carbonaceous residue becomes less and less. By using solutions which contain one-third their volume of strong hydrochloric acid, the ignited residue contains no very objectionable amount of either ferric or chromic oxides, and yet holds all the tungsten. The process may be worked as follows:

To five grams of the sample add 50 grams of cuprammonium chloride crystals, 100 c.c. of hot water, and 50 c.c. concentrated hydrochloric acid. By digesting at boiling point with occasional shaking, the precipitated copper dissolves in about half an hour. Allow to stand a short time longer and filter through paper pulp. Wash with dilute hydrochloric acid, ignite, expel silica with hydrofluoric acid, and weigh. Fuse with sodium carbonate, extract with water, filter, wash, dry, and ignite ferric oxide, etc. If the filtrate has a faint yellow colour, the chromic acid to which it is due may be determined by means of ferrous sulphate and potassium permanganate.<sup>1</sup> It will be found equivalent to not more than one or two milligrams.

When steels containing molybdenum as well as tungsten are treated in this way, the former metal may go wholly into solution on continued digestion, but this is not invariably the case. When the tungsten amounts to about a fraction of one per cent., the treatment at boiling point with solutions containing one-third their volume of strong hydrochloric acid makes the results slightly low. In such cases treatment of the steel with cuprammonium chloride and ten per cent. of acid is preferable.

Part of the silicon passes into solution, and cannot therefore be estimated by noting the loss in weight on treating the ignited residue with hydrofluoric acid.

<sup>1</sup> Each c.c.  $\frac{N}{10}$   $\text{KMnO}_4 = 0.00254$  grams  $\text{Cr}_2\text{O}_3$ .

**The Assay of Tungsten-molybdenum Steels.**

Tungsten may be separated from iron by pouring the acid solution of the two metals into an excess of caustic soda solution in the same manner in which the separation of molybdenum is effected, but the former separation is not by any means so easily made as the latter. It can be made with perfect accuracy when mixtures of standardized sodium tungstate and ferric chloride solutions are poured into a considerable excess of vigorously agitated sodium hydrate, but the nitric acid solution of an ordinary steel behaves differently. In our hands the results so obtained were nearly always one or two tenths per cent. too low, and therefore the contemplated separation of these two metals together from iron by one and the same operation, with the object of subsequent precipitation as lead salts and estimation as on page 85, had to be abandoned. The following process is, however, perfectly reliable :

Over five grams of the sample pour 90 c.c. strong hydrochloric acid and 10 c.c. strong nitric acid. By heating not so strongly as to materially weaken the acids, complete solution is readily brought about. Evaporate to pastiness or even to dryness, but do not bake. Boil with dilute hydrochloric acid (1 in 4), filter off the tungstic oxide and silica, and estimate them in the usual manner. The filtrate contains all the molybdenum, which is separated from the iron with sodium hydrate and estimated as lead molybdate as on page 84. This process has been thoroughly tested (1) by making duplicate assays of tungsten-molybdenum steels, (2) by assaying mixtures of tungsten and molybdenum steels, (3) by assaying mixtures of tungsten steels with fused metallic molybdenum. The following are a few of the results obtained :

Percentage Present.		Percentage Found.	
Mo.	W.	Mo.	W.
2.56	4.50	2.54	4.51
5.67	4.50	5.70	4.51
1.41	4.38	1.40	4.38
Duplicate Assay of		1.76	1.82
Mo - W Steel, -		1.78	1.84

**MOLYBDENUM.****PRELIMINARY SUMMARY.**

Molybdenum is not extensively used in the manufacture of steel, but it is found in this metal often enough to justify the inclusion in this work of a process for its determination. Molybdenum may easily be mistaken for tungsten, and on this account probably occurs in steel more frequently than is generally supposed. Ingleström found as much as nine per cent. of the sesqui-oxide of molybdenum in some varieties of Swedish iron ore, whilst it has also been found in Belgian coal by Armand Jorrison, in pig iron by Ledebur, and in blast furnace refuse by several observers.

Experimenters are by no means unanimous with respect to the influence exerted by molybdenum on the mechanical properties of steel, and, according to our experience of the composition of the commercial alloys of this metal, it would be surprising if they were. Molybdenum powder, the most common form in which the metal is sold for steel-making, is frequently purchased and taken at the vendor's valuation, which is often over-stated in point of actual metallic molybdenum contents to the extent of ten or even twenty per cent. We have, moreover, examined fused alloys of the metal with iron and nickel which contained as much as three per cent. of sulphur. It is therefore possible enough, when such material is used unchecked by reliable analysis, to arrive at conclusions concerning the influence of molybdenum on steel altogether antagonistic to those reached by workers with purer forms of molybdenum or its alloys. This is a sort of disagreement which may be readily eliminated by the diffusion of accurate and not too cumbersome methods of chemical analysis of such materials. The processes described below we believe to be admirably adapted for this purpose, and constitute, at any rate, the only complete descriptions to be found in any English text book.

**Separation from Iron.**—Molybdenum may be separated from iron by fusion of the oxidized sample with sodium carbonate, but also just as accurately and more conveniently by means of aqueous sodium hydrate, in the manner described on page 84. When acid solutions containing molybdenum are evaporated, the trioxide is not left with the insoluble silica unless much tungsten is also present; in such cases small amounts of the oxide may be left on extraction, particularly if the evaporation has been followed by a strong baking. Precipitated

molybdenum trioxide is easily dissolved by dilute mineral acids, but the crystals obtained by sublimation are hardly soluble at all in hydrochloric, nitric, or a mixture of these two acids.

**Gravimetric Estimation.**—Molybdenum may be precipitated from the neutralized or dilute acetic solution of a molybdate by most of the reagents used for precipitating tungsten under similar circumstances (page 76), but it cannot be so readily estimated in the form of the trioxide. The best of such processes is the precipitation with lead acetate solution and estimation as lead molybdate. But precipitation with mercurous nitrate and reduction in a current of hydrogen to the metal or dioxide, or ignition with a known amount of litharge, the increase in weight being counted as molybdenum trioxide, have been suggested by well-known analysts. Molybdenum is volatilized as  $\text{MoO}_3 \cdot 2\text{HCl}$  in a stream of hydrochloric acid, and can then be readily determined as trioxide. The precipitated sulphide may also be ignited to the trioxide after mixing with oxalic acid; or from an acid solution of molybdate a hydrated sesqui-oxide may be electro-deposited.

**Separation from Tungsten.**—All these methods of estimating molybdenum necessitate the absence of tungsten. The most obvious means of separating these two metals is a removal of the volatile trioxide of molybdenum at a red heat, but this is hardly practicable, on account of the tenacity with which the last portions are retained by the tungstic oxide, and the difficulty attending the collection without loss of the sublimed molybdic oxide. The following means have been adopted in practice:

1. Precipitating molybdenum as sulphide from a solution of meta-tungstate; or after adding tartaric acid so as to prevent the precipitation of tungstic oxide on acidifying.
2. Precipitation of the two acids together with lead acetate, mercurous nitrate, etc., and volatilization of the molybdenum in a stream of hydrochloric acid gas: this is an excellent means of making an absolute separation, and has been particularly valuable for special purposes, such as the purification of material for atomic weight determinations.
3. By evaporating with sulphuric acid the tungsten is precipitated, but molybdenum remains dissolved. This is an appropriate separation when molybdenum is to be estimated volumetrically with permanganate.

**Volumetric Estimation.**—Of the volumetric processes the most widely known is Pisani's, in which the acidified molybdate solution is reduced with zinc and titrated with permanganate. The reduced

solution corresponds to the sesqui-oxide, but it is easily oxidized by exposure to air. The titration is most extensively used for the indirect determination of phosphorus in the ammonium phospho-molybdate precipitate (page 53).

The titration of a faintly acetic solution of a soluble molybdate with standard lead acetate, using tannin as indicator, is accurate. It is, indeed, as accurate as the gravimetric process if the tannin reaction is supplemented by filtering off the precipitated lead molybdate and finishing the estimation in the same manner as the Gay Lussac titration of silver with sodium chloride is carried out.

If molybdenum can be obtained as trioxide it may be dissolved in sodium hydrate and titrated with standard acid. Alkaline molybdate solutions may also be distilled with hydrochloric acid and potassium iodide, and the liberated iodine titrated with thiosulphate.

### THE ESTIMATION OF MOLYBDENUM.

It is important to emphasise the fact that when an alkali is added to an acidified mixture of ferric chloride and molybdic acid, a point is reached at which an insoluble basic ferric molybdate is formed, and no perfect separation of the two metals is possible until sufficient alkali has been added to decompose this compound. Similar bodies are formed during the separation of chromic, tungstic, or vanadic acid, from iron.

For the separation of small amounts of iron the excess required need not be a large one so long as the right kind of alkali is used; but as the iron becomes greater the same excess of precipitant becomes less and less able to effect a complete separation. The addition of increasing amounts of alkali improves the separation only very slightly after a certain approximation has been reached, and no system of aerating the precipitated flocks of ferric hydrate, such as using a mixture of sodium hydrate and carbonate, is a material improvement. The power of various alkalis to effect this separation is shown in the following table.

Normal Alkali Added in Excess.	Ammonia.	Sod. Carb.	Sod. Hydrate.
0 c.c.	·0329	—	—
10	·0732	·0936	·1000
30	·0849	·0997	·1002
50	·0890	·0998	·1003

The mixture contained one decigram of molybdenum and two decigrams of iron. The figures given are grams of molybdenum recovered from the filtrate.

The following entirely satisfactory process is not interfered with by any element to be met with in steels except tungsten and vanadium.

Dissolve two grams of the sample in hydrochloric acid, oxidize with nitric acid or potassium chlorate, and add a solution of sodic carbonate or hydrate to destroy all or nearly all the free acid. Care must be taken not to produce a red coloured solution (dissolved hydrate) or a precipitate (basic molybdate). If tungsten is present, or if there is reason to suppose any molybdic oxide has precipitated, then pass the solution through a little pulp and place the filter into a flask containing 30-40 c.c. sodium hydrate of binormal strength in excess of what is needed to precipitate all the iron. This amount is easily calculated, providing the free acid has been neutralized, since one gram of iron as ferric chloride requires 54 c.c. of normal soda to just precipitate it. After breaking up the filter, heat the caustic soda solution nearly to boiling, and then place the flask underneath a funnel with a constricted stem, and shake vigorously with one hand while the hot sample is being poured through the funnel with the other. The molybdenum is all in solution; make up to 500 c.c., filter off a fraction (250 c.c.), add to it a drop of methyl orange and a decided excess of hydrochloric acid. Then add an excess of lead acetate<sup>1</sup> solution, and more than enough ammonium acetate to destroy the free hydrochloric acid. Heat the solution to boiling, allow to settle, filter, wash with hot water, ignite, and weigh as lead molybdate, which contains 26.16 per cent. molybdenum. The separation of the iron is not interfered with by as much as twenty per cent. of either nickel, chromium, or manganese: each is precipitated with the iron.

**Precipitation from Impure Solutions.**—The estimation of molybdenum as lead molybdate is due to Chatard. He, however, invested it with such frailties as it does not really possess; it is, in fact, one of the most stable processes to be found in analytical chemistry. It is not interfered with by the presence of large amounts of acetic acid, lead acetate, or alkaline salts (except sulphates). The paper need not be ignited separately, and prolonged ignition at a much higher temperature than is necessary to destroy the paper does no harm. From faintly acetic acid solution lead molybdate may be

<sup>1</sup> Forty grams of the crystallized salt per litre: 10 c.c. will precipitate a decigram of molybdenum.

precipitated and washed practically free from impurity in the presence of copper, cobalt, nickel, manganese, zinc, magnesium, and mercuric salts.

To the above list we may add barium, calcium, strontium, uranium, arsenic, cadmium, and aluminium by proceeding as follows: add an excess of hydrochloric acid to the solution containing any or all these elements and then the lead acetate. Clear up any precipitate that forms by adding more hydrochloric acid. Then heat to boiling and add more than enough ammonium acetate to destroy the free hydrochloric acid: the precipitate which forms is very granular and easily filtered, washed, etc.

When very large precipitates are formed in impure solutions it is sometimes desirable to re-dissolve the ignited lead molybdate in hydrochloric acid and re-precipitate it. If a precipitate is contaminated with either ferric or chromic oxide the precipitate may be dissolved in strong caustic soda and reformed after filtration.

Always much and sometimes all the tungsten in the acid solution of the steel will be separated from the iron along with the molybdenum, and be precipitated finally as lead tungstate. A separation of the two oxides from their mixed lead salts can be accurately made in the following manner, no matter in what proportion they exist.

Dissolve the ignited lead salts in hydrochloric acid, add a few drops of nitric acid, and evaporate nearly to dryness. Add 100-200 c.c. dilute hydrochloric acid (1 to 4), boil, and filter off the tungstic oxide. Whether the evaporation is made slowly on a water bath or more quickly on a hot plate, some of the tungstic oxide always adheres to the vessel, and cannot be removed by rubbing. It should be dissolved in a little ammonia, and then absorbed by a piece of ashless filter paper and ignited along with the main portion of the precipitate. The molybdenum is re-precipitated from the filtrate with lead acetate, etc.

When tungsten is precipitated with lead acetate from a slightly acetic acid solution the resulting lead tungstate contains all the tungsten, but always less lead than is required by  $\text{PbWO}_4$ . But if it is precipitated along with at least its own weight of molybdenum the precipitate corresponds almost precisely to the calculated  $\text{PbMoO}_4 + \text{PbWO}_4$ , and either one or the other may be determined by difference.



## VANADIUM.

### PRELIMINARY SUMMARY.

The natural occurrence of vanadium in iron and steel in appreciable amounts is so rare, and the purposed addition of it as yet so uncommon<sup>1</sup> that *the* method of estimating it, reliable under the greatest variety of circumstances, has had no opportunity of revealing itself. Many reactions of the metal, however, appear to promise well for the discovery of means for its estimation, in steel-making materials, with accuracy and ease. There is scope for much investigation here, but it must be mainly experimental and not merely speculative; we have been personally much disappointed in the application of processes which *appeared* on the surface to be perfect.

**Separation from Iron.**—Vanadium may be separated from iron by fusion of their oxides with any of the usual mixtures, and also by pouring a partially neutralized solution of their salts into an excess of caustic alkali, in the same way as molybdenum and tungsten are separated from iron. On adding ammonia to a solution of the two metals, the ferric hydrate carries down nearly all the vanadium, apparently as a basic ferric vanadate, but on adding an excess of ammonium phosphate the vanadium is liberated and passes into solution. A similar principle is made use of (Bettendorf) for the separation of vanadium and aluminium, which is a considerably more difficult operation.

When pig iron is attacked by hydrochloric acid, the whole of the vanadium remains in the insoluble residue, and may be obtained fairly pure, after washing out the silica and ferric salts with caustic potash and hydrochloric acid respectively, by ignition of the graphitic residue (Riley). Similarly, when aluminium-vanadium alloys are digested with hydrochloric acid, the whole of the aluminium is dissolved, the vanadium in the residue being unattacked by either hydrochloric acid or alkalis (Helouis).

**Gravimetric Estimation.**—After separating the iron in any of the above-mentioned ways, many possible methods of completing the gravimetric estimation present themselves, always supposing that chromium, molybdenum, tungsten, titanium, phosphorus, and arsenic

<sup>1</sup> Deville observed the improvement of cast iron as being “undoubtedly due to the presence of vanadium,” and devised one of the earliest means of estimating it in such material.



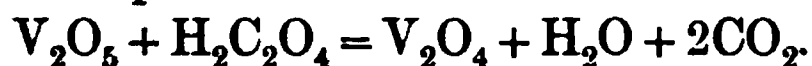
either were not originally present or have been satisfactorily separated. The method most generally known is the precipitation as ammonium metavanadate by saturating the solution with ammonium chloride, and final ignition to pentoxide. The precipitation as metavanadate is liable to lead to contamination with potassium (not sodium) salts, so that such salts should not be used in any previous fusion for the separation of iron.

Solutions of mercuric and mercurous salts, and solutions of salts of lead, bismuth, and barium all completely precipitate vanadium as a vanadate from neutral or faintly alkaline solutions, but as precipitates may also be formed in such solutions by salts of cobalt, nickel, zinc, cadmium, copper, etc., it is evident that the scope of this operation for purposes of estimation is limited.

From an alkaline solution of a vanadate, barium salts precipitate a dibarium vanadate, which may be ignited and weighed as such. From solutions containing free acetic acid, lead acetate precipitates a golden yellow compound, changing on boiling to creamy-white, which corresponds very closely to  $2\text{Pb}_2\text{V}_2\text{O}_7 \cdot \text{PbO}$  even in the presence of considerable excesses of acetic acid, ammonium acetate, or the precipitant. This basic pyrovanadate is generally not considered to be of sufficiently definite composition to justify its being weighed as such, so that either the lead is separated with sulphuric acid, and the evaporated filtrate ignited to vanadium pentoxide, or the vanadium is estimated volumetrically.

When vanadium is precipitated by a solution of uranium nitrate, the precipitate is quite free from the alkaline earths, zinc, manganese, copper, etc., but it may contain phosphorus, arsenic, tungsten, or molybdenum. The ignited precipitate contains 24.2 per cent. vanadium. Solutions of manganous salts also precipitate vanadium quantitatively, even in the presence of molybdenum (Carnot).

In order to obviate the difficulty created by the liability to contamination of the precipitate with other elements in the gravimetric methods just described, it has been proposed to weigh the carbon dioxide evolved on reducing vanadium pentoxide with oxalic acid.



**Volumetric Estimation.**—Nearly all volumetric methods of determining vanadium depend on its reduction to hypovanadate ( $\text{V}_2\text{O}_4$ ) or some lower oxide. An acid solution of the metal is reduced by zinc to  $\text{V}_2\text{O}_2$ , by magnesium to  $\text{V}_2\text{O}_3$ , but by sulphuretted hydrogen, sulphurous acid, ferrous sulphate, some organic acids, hydriodic and hydrobromic acids, etc., to  $\text{V}_2\text{O}_4$  only. With a suitable reducing

agent the amount of vanadium may be measured by the volume added, or by destroying an added excess and measuring the re-oxidation to pentoxide. The oxidizing solution mostly used is permanganate, but other means, such as adding an excess of iodine and titrating the carbonated alkaline solution with sodium arsenite, have also been suggested. Where reduction is effected by boiling the acid solution (often of the precipitated lead or barium salt) with hydrobromic or hydriodic acid, measurement of the liberated halogen is perhaps the readiest means of determining the vanadium.

The reactions of the metal which are known to be serviceable for its colorimetric estimations are :

1. The blue colour of hypovanadate solutions.
2. The brown colour obtained by adding hydrogen peroxide.
3. The sulphovanadite colour formed on passing sulphuretted hydrogen into a caustic alkaline solution.

This last colour was used by Deville for roughly estimating vanadium in cast iron, and it is properly regarded as a delicate and characteristic test. Sulphovanadites are decomposed on acidifying with hydrochloric acid, and the precipitate may be ignited to pentoxide. In former times the colour test was thus transformed into a gravimetric determination.

Other colour reactions are used rather for the detection of vanadium than its estimation. These depend mostly on colours formed with organic bodies, *e.g.* gall, thiocyanate, resorcinol, etc. The best known and most striking is the rapid formation of aniline black when a salt of aniline and a chlorate are added to an acidified solution of a vanadium compound.

### ESTIMATION OF VANADIUM.

As we have said, *the* process for determining vanadium in metals has yet to be discovered ; within their respective limits, however, each of the following acts very well :

#### Colorimetric Method.

This process is carried out exactly like the peroxide colour method for estimating titanium (page 95), except, of course, that a standard solution of vanadium instead of titanium is used to match the colour of the sample. If ammonium metavanadate is used for preparing the standard solution it should be first freed from the ammonium chloride it nearly always contains, by evaporating with sulphuric acid. After

making to a suitable bulk a measured quantity is reduced with sulphurous acid, the excess eliminated by boiling, and decinormal permanganate added to a permanent pink tinge.

$$1 \text{ c.c. } \frac{N}{10} \text{ KMnO}_4 = \cdot 00512 \text{ grams V.}$$

If the hot solution is titrated the first pink tint may be taken as the end point; in cold solutions, however, the permanganate is reduced much more slowly, and a colour which persists for at least a minute should be waited for. A solution may be titrated over and over again by adding sulphurous acid and re-boiling. A standard solution may also be prepared from a previously analyzed ferro-vanadium alloy.

Obviously this method can be used only when titanium is absent. The presence of other metals which give coloured solutions; *e.g.* nickel, copper, and chromium must be allowed for by arranging a standard of similar composition.

### Volumetric Estimations.

1. **Without Separating the Iron.**—In relation to the estimation of vanadium in metallurgical products much importance has been attached to the fact that a solution of hypovanadate is oxidized by potassium permanganate, but not by bichromate. This fact, however, cannot be taken advantage of for determining vanadium in steel, because it is interfered with by the presence of a few grams of iron. Presumably the amount of vanadium should be determined by adding an excess of ferrous sulphate to a solution of steel in which the iron was all in the ferric state, then adding bichromate to extinction of the ferro-cyanide blue, and finally measuring the volume of standard permanganate required to give a pink colour. This is not so: on adding a measured volume of ferrous sulphate to a ferric solution containing a known amount of vanadium the spot test with ferro-cyanide is distinctly blue, or brown for an instant merely and then blue, when bichromate more than equivalent to the excess of ferrous sulphate has been added.

Indeed it is easier, and appears quite feasible, to approximately determine the amount of vanadium in steel by taking advantage of the different rates at which permanganate is reduced by ferrous sulphate and hypovanadic acid respectively. During the bismuthate assay of manganese in vanadium steels (on 1.1 grams) we found that the permanganate used between the point where it diffuses momentarily through the liquid, and the formation of a permanent pink, in each case represented the amount of vanadium present to within a tenth per cent. An

experienced person should have no difficulty in getting within 0·05 per cent. of the true result by proceeding as follows :

Dissolve three grams of steel in 70 c.c. 1·20 nitric acid, and destroy the carbonaceous matter by adding bismuthate as in the assay of manganese.<sup>1</sup> The permanganate formed by the bismuthate, or the manganese dioxide into which it becomes decomposed, must persist on boiling for five or six minutes, so as to thoroughly destroy *all* organic matter. Clear with sulphurous acid, cool, add a small excess of bismuthate, pass through a small filter, and wash with dilute (3 per cent.) nitric acid until the total volume of solution is about 100 c.c. To the perfectly cold solution add an excess of ferrous sulphate and then decinormal permanganate. So long as an excess of ferrous sulphate is present the permanganate, added at the rate of several drops a second, disappears nearly as soon as it touches the solution. When a pink tinge is seen diffused throughout the swirled liquid—though instantaneously only—the reading must be taken. From this point the added permanganate is more and more slowly decolourized, after the manner of hypovanadate oxidations in cold liquids, until a pink colour is practically permanent. In order to allay uncertainty the test may be repeated any number of times merely by adding an excess of ferrous sulphate, and going through the titration in the same way as before.

The operation needs both discretion and judgment, and, except in the hands of a skilled person, the results are only roughly approximate. The volume of solution (100 c.c.), and the rate of adding permanganate and shaking the solution should be kept about constant. The total permanganate used, deducted from the permanganate equivalent of the ferrous sulphate added, gives that due to manganese in the steel.

**2. After Separating the Iron.**—When high carbon steels are dissolved in dilute sulphuric acid most of the contained vanadium remains in the residue. On digesting three grams of fine borings, as in the following process, about 0·10 per cent. of vanadium goes into solution. Rather more is dissolved by stronger acid, or by continued boiling.

Pour 100 c.c. hot dilute sulphuric acid (1 in 10) over three grams of fine borings. Keep the flask constantly boiling and so stoppered that steam may escape, but no air enter. When the iron is dissolved, or nearly so, pour upon a pulp filter, and wash with water. Transfer the filter to a platinum dish, ignite, cover the residue with sodium carbonate, and fuse. Extract the melt with water, filter off ferric

<sup>1</sup>Lead peroxide and sulphuric acid would probably do quite as well as bismuthate if the estimation of manganese is not contemplated.

oxide, etc., acidify the filtrate with sulphuric acid, reduce with sulphurous acid, and titrate with permanganate.

$$1 \text{ c.c. } \frac{N}{10} \text{ KMnO}_4 = 0.171 \text{ per cent. vanadium.}$$

To estimate the dissolved vanadium add 5 c.c. strong nitric acid to the filtrate, and boil to complete the oxidation of the iron and expel nitrous fumes; then add a few cubic centimeters of potassium permanganate (25 grams per litre) to destroy any organic matter. Clear the solution with a few drops of sulphurous acid, make quite cold, add 10 c.c. hydrogen peroxide, and match the colour formed by adding peroxide and standard vanadium to a similar solution of a vanadium-free steel.

Many unsuccessful attempts have been made to prevent vanadium passing into solution. Less is dissolved by boiling with dilute hydrochloric instead of sulphuric acid, but the acid must be driven off by evaporation before the colorimetric test can be applied. By using cold dilute sulphuric acid still less vanadium passes into solution, *i.e.* about 0.02 or 0.03 per cent. Moderately fine borings when agitated by a stream of coal-gas are not decomposed in much less than twelve hours, but the operation may be arranged to take place during the night. The residue, which is fused, etc., as before, always contains much iron ( $\text{Fe}_3\text{C}$ ). We have also decomposed steels with both acid and neutral solutions of cuprammonium chloride, in and out of contact with air; in every case the results were a few hundredths per cent. low, and the filtrate cannot readily be examined.

For general work with hard steels we recommend the decomposition of metals with hot dilute sulphuric acid. Any titanium in a steel or iron should remain in the residue and be separated from vanadium by the sodium carbonate fusion. The following results obtained on six steels tested by

- I. The peroxide colour process,
- II. The volumetric estimation in presence of iron,
- III. Volumetric estimation after separating iron, show that the separate processes lead to concordant results.

	Per cent. Vanadium.					
I.	0.10	0.19	0.40	0.80	1.05	0.68
II.	.12	.19	.44	.80	1.02	—
III.	.11	.16	.44	.76	1.04	.64

When vanadium iron, that is to say, metal containing very little carbon, is treated with acids, nearly all the vanadium goes into solution.

If the percentage is greater than can be satisfactorily determined by colour, a separation may be made in the following manner :

Dissolve the metal in sulphuric acid as usual, add a solution of alum equivalent to about a decigram of the metal, and then ammonia to a faint precipitate. Clear with sulphuric acid, add a small excess of sulphurous acid, boil, and add ammonium acetate carefully until a precipitate forms. Then boil the solution a few minutes, add two or three c.c. more strong ammonium acetate, boil a few minutes longer, and after allowing the precipitate to settle filter through a 12.5 cm. fluted paper and wash once with hot water. Digest the filter and precipitate with dilute sulphuric acid and a little nitric acid so as to dissolve the vanadate of aluminium and decompose the carbide of vanadium which accompanied it. Remove the pulped paper by passing on to a perforated filter plate and cool the solution. Add permanganate to the clear filtrate until a permanent pink tinge forms, and then titrate with ferrous sulphate and permanganate in any of the ways described under Ferro vanadium.

The above separation is not a quite perfect one. Vanadium equal to two or three hundredths per cent. may always be colorimetrically detected in the filtrate. The object of the added ammonium acetate is to destroy the free sulphuric acid only so far as to permit a basic vanadate of alumina to form under the most suitable conditions ; an excess of acetate is undesirable, as it tends rather to engage the aluminium as a basic acetate.

Instead of adding ammonium acetate five or six grams of thio-sulphate may be added and the solution boiled for half an hour. The separation is not quite so good as before, but the filtration is easier, and the precipitate can be washed thoroughly and the vanadium estimated after ignition, either as in the previous case or by fusion with sodium carbonate, elimination of ferric oxide, etc.

## **TITANIUM.**

### **PRELIMINARY SUMMARY.**

It was contended nearly half a century ago that the 'body' and general excellence of certain kinds of steel were due to the presence of titanium ; however that may have been, it is certain that a number of latter-day steels called 'Titanic' are free from that element. Titanium and iron do not alloy very readily ; it is possible to have

several per cents. of titanic oxide in a slag and still be unable to detect the metal in the pig iron it was associated with. Amongst other metallurgical materials it may be found in pig irons occasionally, and in slags, bauxite, fireclay, and ferro-manganese almost invariably.

**The Separation of Titanium from Iron** is very commonly effected by boiling the very dilute and slightly acid solution, with additions of sulphurous acid from time to time, in order to keep the iron in the ferrous state. The acidity of the solution is an important point. According to Levy, the liquid should contain exactly a half per cent. of sulphuric acid and be boiled for six hours; the precipitate is then free from copper, zinc, magnesium, and aluminium, but contains a little iron. On the other hand, the separation is said to be more accurately made when the metals exist as chlorides, but in either case a further addition of acetic acid is sometimes also made. The remaining processes for separating iron and titanium are not easily grouped together.

When iron is dissolved in oxidizing acids the titanium goes partly into solution and remains partly with the insoluble residue. In order to combine the two portions in one small precipitate, the solution may be boiled with sulphurous acid before filtration; or, advantage may be taken of the fact that all the titanic oxide is carried down by a little ferric hydrate precipitated from the bulk of the iron. If, however, the metal contains enough phosphorus, or sodium phosphate is added before evaporating the acid solution to dryness, all the titanium remains with the silica as an insoluble phospho-titanate of iron.<sup>1</sup>

The coloured compound formed by hydrogen peroxide is not so readily carried down by precipitated ferric hydrate, and therefore there are processes for separating the two metals based on the precipitation of iron with peroxidized solutions of caustic soda or ammonia; but the operation needs repeating a few times in order to obtain a complete separation. One of the earlier methods consisted in precipitating titanium and iron together with ammonia, evaporating the solution to dryness, dissolving out the iron with dilute nitric acid or with a mixture of ammonium sulphide and sulphurous acid, and weighing the remaining titanic oxide. In this case, as in many others, it is necessary to separate titanic oxide from silica, and to bear in mind that sulphuric acid must be used with the hydrofluoric in order to prevent volatilization of the former oxide.

A neutral solution of copper potassium chloride leaves all the titanium in the carbonaceous residue. A stream of chlorine passed

<sup>1</sup> Waterhouse (C. N. lxxxv. 198) says that quantitative processes depending on this principle are unreliable.



over heated iron borings volatilizes the silica and titanitic oxide, which may be absorbed in water and separated; the results are said to be higher when thus obtained than when the titanium is carried down by a small basic acetate precipitate (the characteristic feature of what is commonly known as Riley's process). Titanium exists as carbide in pig iron and is insoluble in hydrochloric acid, but easily dissolved by nitric acid (see estimation of graphite, p. 20). By decomposing the iron, therefore, with hydrochloric and treating the residue with nitric acid, all the titanium is obtained free from iron; results obtained in this way are in agreement with those obtained by fusing the acid-evaporated residue with acid potassium sulphate or by volatilizing the titanium with chlorine (Shimer).

**Gravimetric Estimation.**—Titanium may be completely precipitated from pure solutions by means of ammonia or alkaline acetates, but in all cases it is weighed as titanitic oxide; the only exception we know being Apjohn's proposal to weigh as fluor-titanate of potassium. Some other forms in which the element could be weighed are desirable, so that a precipitate might be transformed from one to the other, in order to check results. By the older methods of analysis titanium is one of the most difficult constituents of minerals or metals to estimate with exactness (see Percy, "Fuel," page 121).

**Volumetric Estimation.**—The only volumetric process for estimating titanium depends on the reduction of acid solutions with zinc, and re-oxidation with permanganate. An indirect estimation is possible by this means in the presence of iron, by first reducing with sulphuretted hydrogen or sulphurous acid, and titrating the iron only, and then reducing with zinc and titrating the titanium and iron together.

Pisani, who originated the process, contended that the iron and titanium might be reduced with zinc and then titrated separately, as all the titanium is completely oxidized before any of the ferrous oxide is attacked (the incipient oxidation of the latter is shown by testing with potassium thiocyanate). This contention, however, has been denied.

The best of known methods, and in many ways the most suitable for estimating small amounts of titanium in steel and iron, is the hydrogen peroxide colorimetric process. The yellow colour which hydrogen peroxide forms in nitric or sulphuric acid solutions of the metal will easily detect one part of titanium in a million parts of water; and under the best conditions, using only one gram of steel, will show the presence of less than 0.01 per cent. titanium. But if molybdenum,



vanadium, or chromium can possibly be present the results are less certain, and may be quite unreliable. The colour is also interfered with by hydrofluoric acid, so that solutions of peroxide must be free from this impurity. It is also possible, when the preliminary stages of the test involve an acid potassium sulphate fusion, to have metatitanic acid (which gives no colour with hydrogen peroxide) formed. Dunnington recommends digesting the fusion with five per cent. sulphuric acid to prevent this.

## ESTIMATION OF TITANIUM.

### Colorimetric Method.<sup>1</sup>

This process may be conveniently worked as an adjunct to the bismuthate manganese estimation; the operation is carried out as follows: After completing the manganese estimation discharge the faint pink colour with a drop of ferrous sulphate, transfer the solution to a beaker, and stand it on a white slab by the side of a similar beaker containing a similar iron solution, but no titanium. If the carbonaceous matter was thoroughly destroyed in each case both solutions should have only a faint green tinge. Add 10 c.c. hydrogen peroxide to each; the standard remains unaltered, but the sample becomes yellow if titanium is present. Then run as much of a prepared solution of titanium into the standard as is needed to match the colour of the sample, and from the amount used calculate the percentage in the steel or iron being assayed. It is easily possible in this way to distinguish 0.005 per cent. titanium, and to estimate from this amount up to one per cent. with great accuracy. Metals which form coloured solutions, such as nickel, copper, or chromium, would interfere if some allowance were not made for them. Molybdenum, to a small extent, and vanadium very much interfere with the test on account of the coloured solutions they form with hydrogen peroxide.

*The Peroxide Solution* is prepared by dissolving six or seven grams of sodium peroxide in 250 c.c. dilute sulphuric acid (1 to 3) or nitric acid (1.20), and making up to a litre; it is then of about decinormal strength. Small variations in the amount of hydrogen peroxide used make no difference.

*The Standard Titanium Solution* is prepared by fusing 0.417 grams of pure titanic oxide with sodium carbonate, dissolving up the mixture of sodium titanate and excess of carbonate in a large excess of sulphuric acid (evaporating if necessary), and diluting to 250 c.c. The solution

<sup>1</sup> The colour is supposed to be due to a higher oxide ( $\text{TiO}_3$ ).

should be very freely acid, to prevent any titanous oxide precipitating. Each c.c. of the solution is equal to .001 grams titanium; more dilute solutions are made from it as required. A standard solution is more easily made by dissolving a carefully assayed ferro-titanium alloy in dilute nitric acid.

#### **Gravimetric Method.**

Dissolve five grams of the steel or iron in 30 c.c. hydrochloric acid. If any considerable residue is apparent, then filter, ignite, treat with mixed hydrofluoric and sulphuric acids to drive off the silica, fuse with sodium carbonate, dissolve in hydrochloric acid to a clear solution, and add to the main filtrate. If, however, the hydrofluoric solution is quite clear, that may be at once added to the main filtrate after evaporating to sulphuric anhydride fumes. When the insoluble residue is very small, dilute, as soon as the steel is dissolved, to about 200 c.c., add ammonia until a precipitate forms, which disappears lazily or is just permanent, clear the solution with hydrochloric acid, add ten grams of sodium thiosulphate, and boil for fifteen minutes. Filter, wash by decantation with very dilute (2 to 3 per cent.) hot acetic acid, collect on a pulp filter, and ignite to oxide. The ignited precipitate should be treated with ammonium carbonate and a little water, and re-ignited in order to expel any sulphuric acid, which it retains very strongly. The precipitate is also hygroscopic.

The precipitate may contain small amounts of ferric oxide, silica, alumina, or phosphorus pentoxide. If it can possibly contain very appreciable amounts of the last two it must be treated as the phosphate precipitates of alumina and titanous oxides are on page 123: *i.e.* fused with sodium carbonate. But if these impurities can be present in quite negligible amounts only, then dissolve up the ignited oxide to a clear solution with hydrofluoric and sulphuric acids, eliminate the silica and excess of hydrofluoric acid by evaporation to fumes, and repeat the precipitation in the diluted solution with thiosulphate. The weighed oxide contains sixty per cent. titanium.

### **ALUMINIUM.**

#### **PRELIMINARY SUMMARY.**

**Separations of the Oxides of Iron and Aluminium** depending on either wet or dry treatment with fixed alkalies are well known. The wet separation cannot be properly made, as is sometimes

recommended, by pouring caustic soda into a neutralized solution ; the better way, undoubtedly, is to pour the faintly acid solution into the caustic soda. This operation is extensively practised in the assay of mineral phosphates, but it does not appear clearly whether the separation is assisted by the presence of phosphoric acid, *i.e.* whether the phosphate of alumina is more readily re-dissolved by caustic soda than the hydrate is. A stock objection to caustic soda or potash as well as to the carbonates used in the dry way fusion is, that the alumina they contain needs to be determined and allowed for. Barium hydrate has been suggested to meet this difficulty ; it effects the separation, and can be prepared quite free from alumina. Sodium peroxide can be so used as to temporarily dissolve the iron as well as the alumina, and in this way is very favourable to completeness of the separation. According to Glaser, the peroxide should be added to the nearly neutral and cold solution until it becomes quite clear ; it is then boiled to decompose the sodium ferrate, and the precipitated ferric hydrate is filtered off.

Ammonium sulphide is a better reagent than ammonia for precipitating pure solutions of aluminium ; there is less uncertainty about adding the right excess, adjusting ammonium salts, and so on. In the presence of organic acids, preferably citric or tartaric, alumina is not precipitated, but iron is as ferrous sulphide. Oxalic acid has been used instead of citric or tartaric, but it is only temporarily efficient ; alumina is precipitated on heating.

Other modes of making the separation depending on the precipitation of the iron are :

1. Boiling the neutral solution with freshly precipitated manganese dioxide, whereby the filtrate contains all the alumina (and chromium).
2. Evaporating the nitric acid solution on the water bath, and extracting basic aluminium nitrate with water from the dried mass.
3. Addition of a large excess of trimethylamine, which at first precipitates both oxides, but on long standing completely re-dissolves the alumina.
4. Precipitation from acetic solutions with nitroso- $\beta$ -naphthol ; a reagent which separates iron from nearly every element the steel-works' analyst has to deal with except copper, cobalt, and phosphorus.
5. Some electro-separations : The most interesting is that suggested by Drown and M'Kenna wherein the solution of the steel, freed from carbon and silicon, is electrolyzed in contact with

a mercury cathode ; the iron only amalgamates with the mercury and leaves the aluminium in solution to be precipitated as phosphate or otherwise.

The most useful separations for works' purposes are those in which alumina is the oxide precipitated. One of these, originally designed by Donath, but known both here and abroad by a variety of names, is performed by pouring the reduced iron solution, which is neutral or may contain a small excess of bicarbonate, into a solution of potassium cyanide. When the iron has become transformed to ferro-cyanide the alumina is precipitated by adding ammonium carbonate, or, if free soda is present, by boiling with ammonium chloride or nitrate. This process also separates nickel and cobalt from aluminium.

A process used for mineral phosphates long before there was any notable occasion to estimate aluminium in iron or steel is that described on page 100, *i.e.* precipitation as phosphate by boiling a faintly acid solution with an excess of sodium phosphate and thiosulphate. Without the addition of sodium phosphate the separation is said to be inaccurate unless the solution is boiled for several hours. In any case the time of boiling is variously stated, although to the practical cessation of evolved sulphur dioxide, *i.e.* until all free mineral acid is neutralized, seems a natural ending. Ammonium acetate is sometimes added as well as thiosulphate ; this completely neutralizes the free mineral acid, so that the solution need not be boiled more than a few minutes. The precipitation of neutral solutions is usually represented by the following equation :



When the solution is acid sulphuretted hydrogen is also liberated, and any metal whose sulphide is insoluble is precipitated.

R. T. Thomson (in particular) has worked out a process for determining small amounts of aluminium when associated with large amounts of iron. The ferric solution is reduced with sulphurous acid, an excess of sodium phosphate added, and then, after neutralizing, the aluminium is precipitated as phosphate with ammonium acetate. A small amount of iron, which is also precipitated, is separated by pouring the acid solution of the mixed phosphates into caustic soda and re-precipitating the filtrate with ammonium acetate, etc. Thomson also draws attention to the decomposition of precipitated aluminium phosphate when washed with pure water ; to prevent this it should be washed with a one per cent. ammonium nitrate solution, which also contains a decigram of dihydrogen ammonium phosphate per litre. This process is said to be not interfered with by the presence of titanium ; if much manganese is

present, however, the first separation from the bulk of the iron should be made without adding any sodium phosphate, otherwise manganese is also precipitated.

Ziegler reduces iron to the ferrous state with hypophosphite, and separates the alumina by adding an excess of zinc oxide.

The following processes effect the separation without having to deal at great length with bulky iron precipitates :

1. Treatment of the heated oxides or metals in a current of hydrochloric acid and determination of alumina in the residue. The separation is effected at a lower temperature by mixing a little chlorine with the gaseous acid.
2. Shaking the mixed chlorides with etherized hydrochloric acid, removing the soluble ferric chloride, and igniting the chloride of aluminium under mercuric oxide, or precipitating the aqueous solution of it as usual.
3. Adding phenyl hydrazine to the ferrous solution; this precipitates alumina (and any phosphoric acid) free from calcium, magnesium, manganese, cobalt and nickel, as well as iron.
4. Precipitating the oxides together with potassium oleate and dissolving out the iron soap with hot petroleum.

**Gravimetric Estimation.**—The insoluble forms of alumina filter, wash, and even settle very badly. Particular attention has been paid to the handling of the precipitated hydrate. Precipitates filter better when formed in solutions containing considerable amounts of ammonium chloride or nitrate, but in any case they become sticky on washing with water, and a little is apt to get washed into the filtrate. Washing with a dilute solution of ammonium nitrate not only prevents alumina passing through the filter, but also lessens the ‘packing’ of the precipitate, which is partly responsible for the slow filtration.

Guyard claimed that in the presence of glycerine aluminium hydroxide is precipitated in dense flocks which can be easily washed; but the suggestion does not seem to have been extensively adopted. The fact that less bulky and more easily washed precipitates are obtained by using alkaline bicarbonates is better known; so also is precipitation from a solution of sodium or potassium aluminate, containing only a little free alkali, by passing carbon dioxide; the latter is regarded as a very elegant means of obtaining an easily handled basic carbonate of aluminium.

The presence of ammonium salts not only assists the formation of more easily handled precipitates, but decreases their solubility in an excess of ammonia. The solubility is so far decreased that a small

excess of ammonia need not be boiled off. This avoids dissociation of neutral ammonium salts and consequent redissolving of a little alumina, and at the same time gives a precipitate which is quite free from sulphuric acid. This latter is an important consideration, for alumina is notoriously difficult to free from sulphuric acid by mere ignition.

**Volumetric Estimations** of aluminium are not at all adapted to steel works' purposes. Three processes typical of those known may be mentioned.

1. Titration of sodium aluminate solutions which are neutral to one indicator (phenolphthalein) until they are neutral to another (tropaeolin).
2. Adding an excess of alkali to neutral solutions and titrating the filtrate with standard acid.
3. Adding a standardized phosphate solution, precipitating phosphate of alumina with ammonium acetate and then estimating the excess of phosphoric acid by titration with uranic acetate, etc.

### ESTIMATION OF ALUMINIUM.

Dissolve ten grams of steel in 45 to 50 c.c. strong hydrochloric acid diluted with about its own bulk of hot water. Filter the solution if necessary, add two grams of sodium phosphate, neutralize the solution with ammonia or ammonium carbonate, clear up the small precipitate with hydrochloric acid, and add one or two c.c. in excess. Now add 20 c.c. acetic acid, dilute to 300-400 c.c. with hot water, and when boiling add ten grams of sodium thiosulphate. Boil the solution for ten or fifteen minutes and then filter, wash, ignite, and weigh as phosphate of aluminium.

The precipitate may be pink or even red on account of some iron being carried down. In either case it should be dissolved in a little hydrochloric acid, the solution passed through a small filter to remove silica, and the phosphate of aluminium re-precipitated as before, except that only one gram sodium phosphate need be added, and the other quantities proportionately decreased. The final precipitate should be quite white: it contains 22.1 per cent. aluminium.

The process is interfered with by the presence of copper, large amounts of manganese or nickel, titanium, vanadium, and chromium. Copper may be separated either by sulphuretted hydrogen or thio-sulphate if the solution is kept acid. Any manganese or nickel is eliminated at the second precipitation. Titanium if in small amounts,

can be estimated colorimetrically and allowed for (page 214) or separated as on page 123. Vanadium and aluminium are separated as on page 167, and chromium by fusing the mixed phosphates with sodium carbonate so that aluminium may be precipitated from the water extract with ammonium acetate and sodium phosphate, and chromic acid left in solution.

## COPPER.

### PRELIMINARY SUMMARY.

Copper may be detected in steel by dissolving the sample in acids, adding an excess of ammonia, and looking for a blue filtrate; but, although advocated, this is one of the least satisfactory methods for determining copper. The separation from iron is never perfect; however much the precipitate be washed it always retains copper. The separation is improved, however, by the addition of such alkaline salts as form double compounds with the copper, and if the proper kind and amount are added the separation will be complete, as in the case of nickel (page 72). A better separation is obtainable by evaporating the acid solution and digesting the dried residue with ammonia than by precipitating the acid solution immediately after dissolving.

When iron is precipitated as basic acetate it always retains at least two or three per cent. of the copper present. Even when the neutralization is so carefully made that simple boiling precipitates the ferric hydrate, a little copper also always goes down. Precipitation of the iron by other alkaline salts, whose copper compounds are not so easily decomposed on boiling, leads to good results, *e.g.* the separation is complete if alkaline chromates are substituted for acetates.

If small amounts of copper are associated with large amounts of iron the separation is best effected by precipitating the former. No readier or more perfect means of doing this are available than by boiling the acid solution with thiosulphate. Arsenic, antimony, and tin, or any other metal forming sulphides insoluble in dilute acids would also be precipitated if present; and if the solution is too nearly neutral, or too much thiosulphate is used, the precipitate may also contain the oxides of aluminium, chromium, titanium, or vanadium. The separation may also be made with sulphuretted hydrogen, or its more agreeable substitutes, ammonium sulpho-carbonate, or thio-



acetic acid. If the iron is not already in the ferrous state it should be reduced before precipitating the copper; alkaline hypophosphites have been especially recommended for this purpose.

If the precipitated and somewhat indefinite sulphide of copper is ignited while still moist it is said to pass completely to the oxide; but if dried before ignition the residue is a mixture of the oxide and sulphide, and may also contain small amounts of sulphate. The precipitate is sometimes heated with ammonium carbonate, or in air which has passed through ammonium carbonate solution in order to eliminate any sulphuric acid. The ignited sulphide may be dissolved, freed from small amounts of ferric oxide and silica, and then re-evaporated with nitric acid, but the procedure is open to the objection that, on decomposing, copper is carried away by the evolved nitrous vapours. It is also important to remember that copper oxide is decomposed at high temperatures; it should never be made hot enough to frit, nor should either the oxide or sulphide be ignited over a naked flame unless precautions are taken to exclude reducing gases.

For the separation of co-precipitated arsenic, antimony, or tin it is better to use sodium than ammonium sulphide; the latter always dissolves a little copper and in the presence of molybdenum will dissolve very considerable amounts. When copper is precipitated with caustic soda the excess of alkali is not easily washed out, and, moreover, the operation is prone to be interfered with in a most curious and unexpected manner by certain salts.

### THE ESTIMATION OF COPPER.

Dissolve five grams of steel, or more, according to the amount of copper supposed to be present, in 50 c.c. dilute sulphuric acid (1 to 3). Dilute the solution to 300-400 c.c. with hot water, add five or six grams of sodium thiosulphate, and boil until the milkiness due to precipitated sulphur clears up. Filter through pulp, wash well with hot water, ignite in a porcelain crucible, and weigh. The impurities in the precipitate are silica, ferric oxide, and (from chromium steels) a little chromic oxide.

Dissolve the weighed precipitate in a few c.c. of strong hydrochloric acid, add an excess of ammonia, ignite the collected precipitate, and deduct its weight from the first weighing; the difference, multiplied by 0.798, gives the amount of copper. It is indifferent to the calculation whether the ignited precipitate is regarded as cupric oxide ( $\text{CuO}$ ) or cuprous sulphide ( $\text{Cu}_2\text{S}$ ) since the factor for converting



either compound to metallic copper is the same ; in fact the precipitate is likely to be a mixture of the two.

If the precipitated ferric oxide amounts to more than a few milligrams it must be re-dissolved and re-precipitated before weighing. The two filtrates are then combined, acidified, treated with potassium iodide, and the liberated iodine titrated with thiosulphate as in the determination of copper in alloys. The thiosulphate should be standardized with about the same amount of copper as is being estimated, and under similar conditions.

When steel is dissolved in dilute sulphuric acid only a very small portion of the copper goes into solution, so that quite satisfactory results have been obtained merely by dissolving, filtering, igniting the washed residue, and separating traces of iron, etc., as before. It is as well, however, not to take advantage of this fact unless care is also taken to prevent oxidation of the ferrous solution. When hydrochloric acid is used instead of sulphuric more of the copper goes into solution, but by no means all of it, even with strong acid.

If a distinct precipitate of insoluble chromic oxide remains on treating the ignited precipitate with hydrochloric acid it almost invariably contains copper. To recover this, fuse with a little sodium carbonate, acidify, add 20 c.c. of the dilute sulphuric acid, and re-precipitate the copper with thiosulphate. With high silicon steels the copper oxide may be treated with a mixture of hydrofluoric and nitric acids before weighing; it is then dissolved and the iron separated as usual.

## ARSENIC.

### THE ESTIMATION OF ARSENIC.

Arsenic is frequently separated during a phosphorus estimation, but not often regularly estimated in the daily produce of a furnace, even when it is known to be invariably present.<sup>1</sup> How often an element has to be estimated is of considerable importance in deciding which is the best process for a laboratory to adopt. No exception can be taken to results obtained by the Emil Fischer distillation process when carried out in such a manner as that described by Mr. Stead (*Journal Iron and Steel Inst.* 1895, i. 110), and no further process need be looked for if

<sup>1</sup> Tables are given by Pattinson and Stead (*Journal of the Iron and Steel Institute*, 1888, i. 171), showing the proportion of arsenic in ores, pig irons, and ferro-manganese.

arsenic estimations are the order of the day, or are made so regularly even that the necessary apparatus can be kept at hand. But where a month or a year intervenes between one estimation and another of any element, a process requiring special apparatus is more or less unsuitable. On this account we propose the following procedure for the estimation of arsenic in steel and iron.

Weigh five grams of steel into a stoppered flask fitted with a Will and Varrentrap (or some other simple) absorption bulb (Fig. 9). Add 30 c.c. hydrochloric acid diluted with nearly its own bulk of hot water,

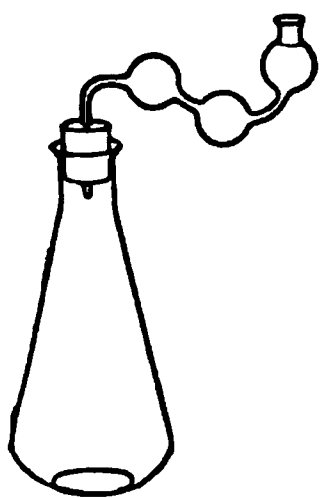


FIG. 9.

quickly replace the stopper, and heat to very gentle boiling until the steel is dissolved. Then boil more vigorously until the few drops of bromine (which are kept in the middle absorption bulb in order to renew the strength of the overlying bromine water) are dissolved. A portion of the arsenic passing off as gas is retained in the Will and Varrentrap, a portion passes into solution, and the remainder, in the form of metallic arsenic or arsenide of iron, is seen as a graphitic-looking scum over the surface of the liquid and sides of the flask. The amount passing off as

gas varies from five to fifteen per cent. of the arsenic present, according to the rate at which the metal is dissolved. If a series of steels containing small amounts of arsenic were being assayed it would be feasible, unless great accuracy was required, to omit the absorption bulb and make a suitable correction.

Cool the solution after the steel is dissolved, and add 5 c.c. concentrated hydrochloric acid and about half a gram of pure zinc sulphide. Then stopper the flask so as to retain the evolved sulphuretted hydrogen under slight pressure, and shake for two or three minutes before allowing the precipitate to settle. Collect the mixed precipitate on a pulp filter, and wash with five per cent. hydrochloric acid. Split the pulp filter, return the part carrying the precipitate to the original flask, add seven to ten cubic centimetres hydrochloric acid and the bromine water from the Will and Varrentrap. Break up the filter by shaking, and, if necessary, add more bromine until a slight excess is present. Strain off the paper through the remaining half of the split filter, and wash with small amounts of water, so that the volume of the filtrate may not exceed 70 c.c.

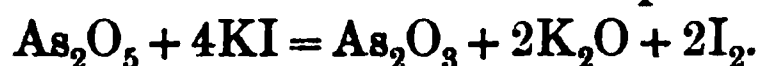
Heat the solution to boiling, and drive off nearly all the free bromine. Add four or five pea-sized crystals of potassium iodide, and 5 c.c. sulphurous acid of B.P. strength in excess of that needed to destroy the

free bromine and iodine. Boil off the excess of sulphurous acid, cool, add half a gram of zinc sulphide and collect the precipitated arsenious sulphide on pulp as before. Very little washing is needed.

Split the filter as before, return the upper portion to the flask and add 10 c.c. of a normal soda solution which has been saturated with sulphuretted hydrogen, and shake so as to break up the filter and promote the complete solution of the arsenious sulphide and the separation of the very small amounts of sulphides of iron (and copper). A gram or so of ammonium chloride is added so as to make the insoluble sulphides filtrable, and the washing is done with water containing a pinch of the same salt and a drop of ammonia.

The filtrate is neutralized, about one-tenth its volume of strong hydrochloric acid and a slight excess of bromine water added, and then a few crystals of potassium iodide and the excess of sulphurous acid as before.

The above reductions to arsenious acid take place as follows :



Sulphurous acid destroys the free iodine, and thus accomplishes the reduction of still more arsenic acid. In this way solutions of both arsenic and antimony may be reduced with less than the theoretical amount of potassium iodide under such conditions as do not permit sulphurous acid alone to effect reductions. Free iodine will colour the solution if all the sulphurous acid is boiled off before the reduction is completed ; in any case a crystal of potassium iodide dropped into the hot solution should give no permanent colour.

When the solution is free from sulphurous acid and quite cold, add 2 c.c. clear starch liquor and one or two drops of standard iodine. If more than two drops of iodine solution are needed it is an indication that all the sulphurous acid has not been boiled off ; but this causes no difficulty if iodine is added until a distinctly blue colour persists. If a strong solution of caustic soda or ammonia be now added the disappearance of the colour corresponds very nearly with the neutral point. Go back to faint acidity, add 20 c.c. in excess of a saturated solution of sodium bicarbonate, cool again if necessary, and titrate with standard iodine.

The iodine solution is prepared so that each c.c. corresponds to 0.01 per cent. arsenic, when five grams of steel are used, by dissolving 1.7 grams of re-sublimed iodine with two or three grams potassium iodide in water and making up to a litre. The solution is practically constant if kept in a stoppered bottle away from the light, but it may be checked against a solution of sodium arsenite, which should be of

equal strength if made as follows: Dissolve 0.66 grams of arsenious oxide along with four grams of sodium carbonate in boiling water and make up to a litre.

**The hydrochloric acid** is apt to contain small amounts of arsenic; it should be tested by adding 20 c.c. of a clear strong solution of stannous chloride to 50 c.c. of the acid. A dark brown precipitate or coloration due to arsenide of tin condemns the acid: this is Bettendorf's test. The acid may also be tested by saturating it with sulphuretted hydrogen or adding zinc sulphide. One part of arsenic (existing as arsenious chloride) in four hundred thousand parts of acid of 1.17 specific gravity is distinctly visible as precipitated sulphide (Pattinson).

Although the above process involves a large number of operations they are of so simple and quickly-executed a kind that it takes no longer than the distillation process, even when the necessary apparatus for the latter has been prepared. Tests made by adding known amounts of arsenious oxide to arsenic-free steels gave excellent results, and repeated assays of the same arsenical metals were very concordant.

## IRON.

### PRELIMINARY SUMMARY.

An accurate gravimetric estimation can be speedily made only when the element is present in practically pure solutions. The precipitation commonly practised, *i.e.* as hydrate, is a form hardly distinctive enough for the estimation of iron in the presence of those metals it is commonly associated with. A large number of elements, such as phosphorus, arsenic, tungsten, molybdenum, vanadium, etc., form fairly stable iron compounds in neutral or faintly alkaline solutions. In addition to these elements, which are really precipitated by the iron itself, there is another class, including nickel, cobalt, copper, potassium, etc., which appear to be carried down through absorption by the ferric hydrate without forming actual compounds. Volumetric processes are, therefore, more trustworthy for general use.

**Volumetric determinations** may be separately considered according as a ferrous or ferric solution is titrated.

Ferric solutions can be reduced with zinc in a variety of ways. In the ordinary or amalgamated forms it is used in an acid solution, and either completely dissolved or filtered off. The reduction is so rapid that mere filtration through a column of the finely divided metal

transforms the ferric iron completely. Powdered zinc or magnesium is also used in the dry way by heating with mixed oxides, and dissolving out the reduced iron. Occasionally an interfering metal, such as copper, may be eliminated by the wet reduction, but other metals, such as tungsten, molybdenum, vanadium, and titanium should be absent as they are reduced to lower oxides.

Ammonium sulphide and sulphuretted hydrogen are very effective reducing agents. They precipitate some interfering metals, and do not form lower oxides of others so readily as zinc. Excess of sulphuretted hydrogen may be completely boiled off, or the last traces precipitated with mercuric chloride. Precipitated sulphur has no effect on the permanganate titration.

Stannous chloride is a particularly useful reagent in dealing with work of a known kind. Unlike sulphur dioxide it effects the reduction in very acid solutions. An excess of the reagent can be destroyed by adding mercuric chloride. A solution of sodium phosphate is sometimes also added, so that the colour of the ferric chloride, reformed during the titration, may not interfere with the permanganate end reaction. Stannous chloride also reduces other metals sometimes associated with iron: molybdenum, for instance, and platinum which may be carried into solution from a preliminary fusion.

The direct titration of ferric solutions, and the conditions under which they give accurate results, have been extensively studied, but not adopted in works' laboratories, with the exception of the direct stannous chloride titration. This operation is performed in very acid solutions, and is at an end when the ferric chloride colour disappears. A known amount of copper chloride may be added to heighten the end reaction; or a mixture of mercuric and platinic chlorides added, and the precipitation of a dark cloud of the reduced metals looked for.

The earliest direct determination of ferric iron was made by adding an excess of sodium thiosulphate to the neutralized solution and titrating with iodine and starch; or what amounts to practically the same thing, the faintly acid solution was titrated with hyposulphite after adding potassium iodide. Distillation of the acidified ferric chloride with potassium iodide is a more elaborate form of the same process. A rather fanciful modification is to heat ferric chloride and potassium iodide along with metallic mercury, and to determine by loss the amount of the latter which has combined with the liberated iodine; and from that the proportionate amount of iron.

Acid solutions of ferric chloride may be titrated with thiosulphate in the presence of potassium thiocyanate, the end reaction being

then determined by the disappearance of the deep red colour. In the presence of thiocyanate the titration can be made with cuprous chloride, which forms a cloud of cuprous thiocyanate when all the iron is reduced.

According to Carnot the most effective reagent for oxidizing cold ferrous solutions is hydrogen peroxide.

### THE ESTIMATION OF IRON.

If the amount of iron in steel is considered at all, the percentage is usually determined by subtracting the sum of all the other elements from 100. When comparatively pure iron and ordinary grades of steel are being dealt with, this procedure is quite as accurate if not more so than a direct determination would be. The assay of large amounts of iron is practised generally with fewer refinements than the assay of more expensive metals.

From the large number of volumetric methods, we propose to describe and consider the reduction with sulphurous acid or alkaline sulphites and titration with bichromate or permanganate. It is perhaps not so speedy as some others, but it appears to be interfered with less by the presence of foreign elements.

**Reduction to Ferrous Oxide.**—Sulphurous does not effect a speedy or complete reduction in the presence of much free acid; add ammonia, therefore, until the darkening colour shows that all free acid has gone. Then add an excess of sulphurous acid, heat until the solution becomes colourless, acidify, and boil. The boiling should be continued several minutes after the sense of smell can no longer detect sulphur dioxide. A supplementary test, easily applied, and not interfered with by colds or other physiological derangements, is to place an acid solution of very dilute permanganate under the longer leg of the bent tube as in Fig. 10. The formation of a

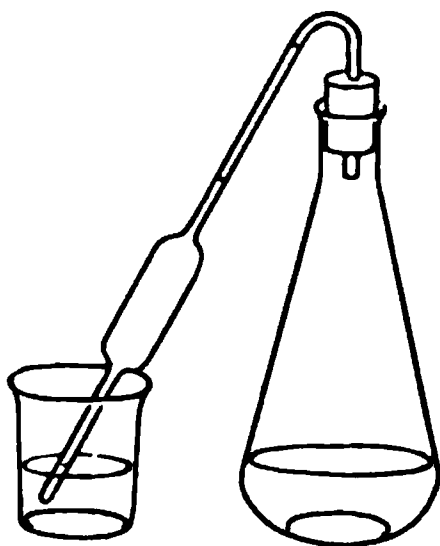


FIG. 10.

brown turbidity may be disregarded, but a clearing of the solution indicates sulphurous acid. On account of the large volume of steam condensed in the permanganate the test is a very delicate one.

It is necessary sometimes to digest a solution short of boiling until the reduction is complete. It is generally complete some time before boiling point can be reached, however the flask be heated; but when some other metals besides iron are present the reduction proceeds more

slowly, and without the above precaution it is easy to drive off the excess of sulphur dioxide and leave a mixture of ferrous and ferric iron in solution.

When the last trace of sulphur dioxide has been expelled, substitute an emulsion of sodium bicarbonate in recently boiled water for the dilute permanganate, and cool the flask under the tap, taking care to control the ascent of the carbonated liquor by pinching the rubber connection.

**Titration.**—Titration with standard permanganate is the readiest means of determining the reduced iron; it is desirable, however, to have little or no hydrochloric acid in solution unless salts of some other metals are added to prevent it reacting with permanganate. Manganous sulphate is commonly used for this purpose, but salts of lead, mercury, magnesia, etc., have also been recommended. This means of estimating iron is not interfered with by the presence of any element commonly associated with steelworks' materials except vanadium.

Bichromate may be used with either hydrochloric or sulphuric acid solutions, but the end reaction is sharper in the latter. The ferri-cyanide indicator develops the blue colour rather slowly with very dilute ferrous solutions, so that a premature finish is generally obtained. This error is not a serious one, and is eliminated if the bichromate solution is standardized in the same way. In order to reach a true finish the mixed test drops should be covered with a porcelain crucible, so as to shut out the light, and allowed to stand a few minutes. Ferri-cyanide solution should be freshly prepared; a very short exposure to direct sunlight may cause it to give a blue colour with ferric salts.

The bichromate titration may be interfered with by a number of commonly occurring elements; any element in fact which can form insoluble ferri-cyanides. The presence of considerable amounts of manganese, for instance, as in Stead's modification of the process for estimating chromium (page 62), gives a brown colour with the indicator, which may mask the reaction with dilute ferrous solutions. Nickel and copper act similarly. The interference can usually be overcome by using very dilute acid solutions of ferri-cyanide, so that insoluble compounds of the foreign metal cannot form.

**Standard Solutions.**—A bichromate is more stable than a permanganate solution; still the comparison is not so unfavourable to the latter as many people suppose. When prepared and preserved with reasonable care a decinormal permanganate solution may be kept unaltered for months. Commercial permanganate crystals always contain a little manganese dioxide, which causes a spontaneous



decomposition, with liberation of oxygen, even in the cold. This explains why many standard solutions gradually lose strength; it also suggests the remedy, viz. to carefully filter the solution through recently ignited asbestos before making up to the required volume.

The method most used for standardizing both permanganate and bichromate solutions consists in dissolving a carefully weighed amount of fine and nearly pure iron wire in dilute sulphuric acid, and noting the volume of solution needed to just oxidize it.

As the best iron wire is not chemically pure an allowance of from two to four-tenths per cent. is usually made for impurities, that is to say, the weight of wire taken is multiplied by from 0.996 to 0.998 in calculating the permanganate's strength. This correction obviously involves the assumption that the impurities simply diminish the amount of iron really present, and have no other influence upon the process. It has been shown, however, that this assumption is entirely wrong, that the small particles of carbon to be seen floating in solution are oxidized by the permanganate, and that a positive correction of from one to two per cent. may need to be made. The low atomic weight of carbon helps to explain the surprisingly large correction.

The importance of having a correct standard solution for other purposes besides the estimation of iron makes it desirable to quote Mr. Irby's experiments on the above point. "A solution of permanganate was prepared, which, standardized by pure oxalic acid, was found to be of such strength that a decigram of iron would require 18.15 c.c. 1.0407 grams of bright, fine pianoforte wire was dissolved in dilute sulphuric acid, and after well mixing was allowed to stand until the small black flocks had settled to the bottom of the flask. The flask and contents were weighed, and three successive portions of the clear solution were decanted, clear of carbon, into other flasks; the remaining portion of the solution contained all the carbon.

"The amount of permanganate decolourized by each portion was determined, care being taken throughout to prevent atmospheric oxidation:

Portion.	Weight.	KMnO <sub>4</sub> required.
I.	13.125 grains.	52.05 c.c.
II.	12.887 „	51.20 „
III.	11.618 „	46.15 „



Hence a decigram of iron was equal to 18·20, 18·25, and 18·25 c.c. respectively; these agree with the determination by means of oxalic acid (18·15 c.c.).

“The fourth portion of the iron solution containing the suspended carbon weighed 10·032 grams, and required 43·7 c.c. permanganate, although calculating from the mean of the preceding figures it should have taken only 39·83 c.c. On reducing the ferric sulphate by means of zinc and re-titrating it actually took 40·0 c.c. permanganate. Thus the carbon of the 1·0407 grams of iron wire reduced 3·7 c.c. of permanganate, and did the work of ·0203 grams of iron, or introduced an error equal to 1·95 per cent.”

A similar error, though perhaps of less magnitude, attaches to the like standardization of bichromate solutions. It is, therefore, necessary when iron is used for standardizing either permanganate or bichromate solutions to destroy the organic matter due to the carbon, or, if merely titrating the sulphuric acid solution is considered to be sufficiently accurate, to make no correction for impurities.

## MINOR CONSTITUENTS OF STEEL.

In addition to the elements already dealt with steel may contain small amounts of other elements which are rarely looked for.

**Antimony and Tin.**—These metals may have existed in the ore or have been introduced by charging tin plate scrap into the furnace. Both may be separated with sulphuretted hydrogen from ten or twenty grams of the sample dissolved in hydrochloric acid. The precipitated sulphides may also contain copper and arsenic. The required separations and the manner of making the determinations may be learnt from a study of the section on white metal alloys. Simple and accurate processes for the regular estimation of these constituents could readily be devised if necessary.

**Slag and Oxides.**—Slag can occur in well fused steels in small amounts only, and then but locally; it is not a constituent that can be regularly estimated to any purpose.

Oxygen is known to exist in steels—particularly very low carbon steels—in the form of ferrous oxide or oxides of the other constituent metals. Its determination is said (Ledebur) to be almost as important as that of sulphur and phosphorus, but it is doubtful whether a process approaching satisfaction is known. Ignition of the metal in hydrogen

and estimation of the water formed, which is the most exact process, is not only troublesome, but also subject to error through occluded slag, etc. Those especially interested should look up Nos. 202, 223, 281 and 281 *a* of the bibliography.

**Nitrogen.**—Mr. A. H. Allen applied the Nessler test to the estimation of nitrogen in steel as early as 1872. His papers dealing with the subject are to be found in the *Journal of the Iron and Steel Institute*, 1879, 480, and 1880, 181; also in the *Chemical News*, xli. 231. A modification, by Langley, of Allen's process is given in Blair's *Chemical Analysis of Iron*. The existence of nitrogen in irons other than in the occluded state is an interesting fact, but it appears to have no practical significance, and its determination is therefore very rarely attempted.<sup>1</sup>

**Calcium and Magnesium.**—These elements are said to occur in iron and steel, but it is doubtful whether the usual methods are refined enough to determine them, even supposing the results were found to have any value.

**Silver and Gold.**—These elements have been found by Warren in Swedish and Lowmoor irons, as well as in some varieties of steel. Spectroscopic traces of other (rare) elements have been found in steel, irons, and ores.

**Uranium.**—This element has been added to steel by French experimentalists, and found to influence its physical properties in a similar manner to, but surpassing nickel; it is also in use at some continental ordnance works. Uranium may be separated from iron either by the ether extraction process or by boiling with a large excess of sodium carbonate. Various modes of making other separations, and the subsequent determinations, are lengthily discussed by Kern (*Journ. Amer. Chem. Soc.*, xxiii. No. 10, and *Chemical News*, lxxxiv. 224).

<sup>1</sup> See also Baker, *C. N.* x. 245 and Harboard and Twynam, *J. I. S. I.*, 1896, ii.

## PART II. THE ANALYSIS OF PIG-IRONS.

THE methods used for the analysis of steel are in most cases applicable to pig-iron; only a few differences therefore need be noticed.

### Carbon.

Liberation of carbon and dry combustion exactly as for steels. With a good furnace graphite is readily burned in air, but making allowance for poor furnaces and deficient gas supplies it is safer to recommend combustion of the total carbon in oxygen. Direct combustion with red lead (page 9) is particularly suited to the estimation of carbon in pig-irons, because the borings are always fine ones. Sievings are invariably richer in carbon (graphite), and could not be accepted in any case as a fair sample.

Graphite is estimated as in steels (page 20). When the pigs are so highly siliceous as to retard filtration, a few drops of hydrofluoric acid may be added to destroy the silica or leucon.

### Silicon.

As for steels. Ignition of the siliceous residue needs to be prolonged to burn off graphite: a stream of oxygen projected into the mouth of the crucible has been suggested as a means of hastening the ignition. The silica should always be volatilized with hydrofluoric and sulphuric acids, so that any unburned graphite or small residue of titanite or ferric oxide may be observed.

### Manganese.

May be estimated as in steels either gravimetrically or volumetrically. The red lead process is available only for pigs low in manganese, and then not always with perfect satisfaction. The bismuthate gives accurate results if the graphite is filtered off and the hot solution then treated with bismuthate. The solution should be kept at boiling point for some time after the permanganate formed has decomposed to manganese dioxide. With white irons in particular the dissolved organic matter appears to be not so readily destroyed as in steels.

### **Sulphur.**

As for steels. The gravimetric process only should be employed except in comparative tests. There are very rare cases where all the sulphur cannot be determined even by the gravimetric process as usually carried out. It is then necessary after evaporating to dryness and baking, to test the residue, insoluble in hydrochloric acid, by igniting with a little of the mixture used for estimating sulphur in coke (p. 233). Possibly the reason why all the sulphur cannot be extracted from coal by digesting with acids may also explain the exceptional behaviour of these pig-irons.

### **Phosphorus.**

If the pig is a very siliceous one add a few drops of hydrofluoric acid, filter off the graphite, and finish like an ordinary steel. Less than two grams may be weighed off and the process modified accordingly when the phosphorus is known to be high; but when the precipitated phospho-molybdate is the earliest indication that much phosphorus is present, it should be washed and dissolved in ammonia as usual; the solution is then made up to a definite volume, and only a fraction of it used to form lead molybdate. There is little advantage, and there may be trouble in having a final precipitate weighing more than a half or three quarters of a gram.

For the determination of phosphorus in pig-irons containing titanium see page 172.

### **Titanium.**

The colorimetric determination is made, as for steels, on the solution used for the bismuthate estimation of manganese. The graphite, silica, etc., filtered off contain no titanium; at least we have never detected any by fusing the ignited residue with sodium carbonate, dissolving in acid, and adding hydrogen peroxide, although the pigs contained considerable quantities. In the gravimetric process (page 96) all or nearly all the titanium would remain undissolved with the graphite.

### **Vanadium.**

This element may be estimated by either of the methods used for steels. British chromiferous pig-irons invariably contain vanadium (Stead). If the peroxide test is used the colour must not be confused with that given by titanium. One is red, the other yellow: moreover the colour of vanadium solutions disappears on boiling, that of titanium solutions does not; but if both are present together the colour disappears entirely.

## PART III. THE ANALYSIS OF STEEL-MAKING ALLOYS.

### SILICON ALLOYS.

#### FERRO-SILICON AND SILICO-SPIEGEL.

##### Total Carbon.

THE powdered alloys are scarcely attacked at all by cold, and only partially by hot copper solutions.

They are easily and completely decarbonized by ignition in a stream of oxygen either with or without such oxidizing agents as copper oxide and lead chromate. It is better to dispense with these reagents when possible, because there is then no blank determination to be done; and no metallic beads, with the attendant possibility of occlusion of some unattacked material, are formed. As there is no actual fusion, the same boat is available time after time. The ferro-silicon after ignition is powdery or is easily crumbled; silico-spiegel is fritted into a single piece.

##### Graphite.

The carbon in ferro-silicon exists chiefly as graphite, the combined carbon amounting to a few tenths per cent only.

	"Lonsdale."	"Ayresome."	"Mostyn."
Combined carbon, -	0·20	0·15	0·19
Graphite, - -	1·39	1·39	1·62
Silicon, - - -	12·32	13·28	12·08

The graphite is determined as follows, combined carbon being obtained by difference. Two or three grams of the powdered alloy are covered with 70-100 c.c. of 1·20 nitric acid and the liquid heated nearly to boiling. The reaction with ferro-silicon is very slight, but on adding

next a few drops of hydrofluoric acid the reaction becomes very vigorous, and is maintained by adding from time to time further small quantities of hydrofluoric acid until particles of graphite only are to be seen. The action should not be hurried, but time allowed for the flocks of the nitrated (combined) carbon compound to dissolve before any considerable excess of hydrofluoric acid is added. The decomposition can be effected in the same glass flask time after time without damaging the vessel. This is an advantage, as it allows the course of the reaction to be observed and the complete decomposition of the alloy to be readily determined. The residue is filtered through asbestos, washed with water, then with boiling sodium hydrate (2N), then once with dilute hydrochloric acid, and finally with water until the washings give no reaction with silver nitrate solution. The residue is then burnt in a current of oxygen in the usual way.

Donath and Hailsig (*Stahl und Eisen*, xvii. 670, and *Journal of Iron and Steel Institute*, 1897, ii. 488) examined a ferro-silicon which contained 14·3 per cent. of silicon, and as much as 1·39 per cent. of combined carbon, which the authors believed was present in the alloy as silicon carbide (carborundum). In the process given for estimating silicon (p. 117) carborundum, if present, would be collected with the silica, and after treatment with hydrofluoric acid would still remain undecomposed. This residue, however, in our experience, never exceeds two or three milligrams, and consists chiefly of ferric oxide, so that generally the existence of carbide of silicon, except in high grade alloys, is very unlikely.<sup>1</sup>

The total carbon of silico-spiegels is generally greater than that of ferro-silicon and contains more combined carbon. As before, the graphite is estimated after decomposing the sample with nitric and hydrofluoric acids, and the combined carbon obtained by difference.

Combined carbon, -	1·41	1·89	1·61	1·31	0·51
Graphite, -	0·77	0·34	0·94	0·60	1·22
Silicon, -	—	10·53	10·95	12·13	13·34
Manganese, -	—	19·85	18·14	18·25	20·20

### Silicon.

The chief difficulty in the analysis of these alloys for practical purposes lies in the decomposition of the sample. Boiling with

<sup>1</sup> Carnot and Goutal (*Journal of the Chemical Society*, lxxiv. ii, 590) find the silicon in ferro-silicon to exist as  $\text{Fe}_2\text{Si}$ , in silico-spiegel as  $\text{Si}(\text{Fe. Mn})_3$ , and in ferro-manganese as  $\text{SiFe}_2$ .

brominized hydrochloric acid, aqua regia, or hydrochloric and sulphuric acids are the common methods of attacking the sample in the wet way. It is maintained by some analysts that these alloys cannot be thoroughly decomposed in any of these ways with anything like the ease and convenience which attends fusion with acid potassium sulphate, sodium carbonate with nitre, or sodium peroxide. This opinion is mainly based on certain observations which were explained by Hogg.

The misconception that ferro-silicon and silico-spiegel cannot be completely decomposed by aqua regia, for instance, has arisen from two causes. In the first place, if the alloy be not finely powdered, the particles become coated with silica, and further decomposition is thereby stopped; and secondly, even if the alloy is sufficiently finely divided, the evaporation to dryness and gentle heating followed by treatment with hydrochloric acid always gives a silica contaminated with oxide of iron. The most obvious inference is that the alloy was only partially decomposed; this, however, is not so. According to Hogg, the peculiar physical condition of the silica is the cause of its taking up and firmly retaining some ferric oxide.<sup>1</sup> To reduce this source of contamination to a minimum, the separated silica should be filtered off after dissolving, the filtrate being then evaporated to dryness to recover the small quantity in solution.

Hogg finds, and the conclusion is supported by much independent testimony, that the silica which passes into solution is much greater with low than with high percentage alloys. For alloys containing 10 to 15 per cent. of silicon, he finds the soluble portion to be between 0.1 and 0.3 per cent., and this amount he does not recover, adding by way of correction 0.2 per cent. to the amount obtained by filtering off immediately after decomposition. A large number of test analyses enables us to confirm Hogg's conclusions in every particular except the minor one referred to in the following account of the process.

Grind as much of the sieved sample as is needed for the assay in an agate mortar, weigh off two grams, add 50 c.c. concentrated hydrochloric acid and 10 to 20 c.c. nitric acid. Boil to decomposition, which is complete in about 15 minutes, add about twice the volume of water and *filter at once*; wash with cold dilute hydrochloric acid, ignite and weigh. The silica is invariably white, and the residue after treatment with hydrofluoric acid will be found not to exceed two or three milligrams.

<sup>1</sup> The presence of graphite may also be suspected as the cause of the insoluble ferric oxide. The "physical condition of silica" explanation should not be insisted upon until alloys free from graphite have been experimented with.

To the result obtained add only 0.1 per cent. as a correction for the soluble silica.

The amount of silicon which dissolves is increased by boiling the solution after diluting. After dilution and allowing to stand on a hot plate for two hours, 20 to 30 milligrams of silica were found dissolved, so that the correction of 0.1 per cent. applies only to the conditions stated. The silica as weighed is in a very fine state of division, and it is also very hygroscopic. Hillebrand (*Chemical News*, lxxxiii. 136) states that blasting for nearly half an hour is necessary to expel all the moisture from silica, and it is then not hygroscopic.

#### **Manganese.**

The manganese in ferro-silicon may be so small in amount as to be determined by the red lead process (p. 32). The manganese in silico-spiegel (as well as that in ferro-silicon) may be determined by making an acetate separation of the iron in the filtrate from the silica and estimating as  $\text{Mn}_3\text{O}_4$ ; or titrating the manganous acetate solution with permanganate according to the process described on p. 126. The manganese in either alloy may also be assayed by the bismuthate process if they are first got into solution by weighing off 1.1 grams of the powdered sample and adding 50 c.c. nitric acid (1.20) and 2 or 3 c.c. of hydrofluoric acid. After filtering off the graphite, the procedure for ferro-silicons is the same as that for pig-irons (p. 113), and for silico-spiegels the same as that for manganese alloys (p. 127). No interference with the process is exerted by the presence of the hydrofluoric acid. Needless large amounts of this acid, however, cause the final permanganate tint to be readily converted into manganic oxide through the agency of the manganous fluoride in solution.

#### **Sulphur.**

This element can be estimated gravimetrically as in steels, using 2.5 grams of the sample.

#### **Phosphorus.**

The process used for steel cannot be directly applied to the estimation of phosphorus in these alloys, because they are not decomposed by 1.20 nitric acid. By decomposing them with nitro-hydrochloric acid and evaporating so as to dehydrate the silica and eliminate hydrochloric acid, a portion of the phosphorus always remains with the silica. This may constitute a source of very serious error when highly phosphoretted material is being assayed; e.g. of the 0.20 per cent. of phosphorus in a certain silico-spiegel, 0.063 per cent. was found with



the ignited silica. An obvious means of minimizing, if not actually eliminating, this error, is to filter as soon as the sample is decomposed, as in the estimation of silicon, and use the evaporated filtrate for estimating the phosphorus.

These alloys being readily decomposed by mixtures of nitric and hydrofluoric acids, a removal of the silica with excess of the latter, would at once allay all fear of loss of phosphorus, but the precipitation of phosphorus as ammonium phospho-molybdate is by no means insensible to the presence of hydrofluoric acid. Very small amounts of this acid retard the precipitation, and large amounts prevent it altogether. By preparing identical solutions of the same steel which contained 0.064 per cent. of phosphorus, and adding 1.7, 3.4, and 5.1 c.c. of hydrofluoric acid just before adding the molybdate reagent, the first was found to precipitate almost at once, but the second and third showed no signs of a precipitate for some time. After standing, however, for two hours at about 60° C., the filtered precipitates were converted to lead molybdate and were found to correspond to 0.060, 0.063, and 0.061 per cent. of phosphorus.

Along with the usual amount of nitric acid, a ferro-silicon or silico-spiegel can be easily decomposed by using no more than 4 c.c. of hydrofluoric acid for two grams of the sample; the small quantities of this acid left unused by the silicon are nearly all expelled by the subsequent boilings, so that a series of tests in which silica was added to the above-mentioned steel dissolved in nitro-hydrofluoric acid showed no signs, when the phosphorus was precipitated, of lagging, and the completion of the estimations yielded 0.065, 0.063, 0.064, and 0.066 per cent. instead of the 0.064 of phosphorus actually present. Under these circumstances it is evident that the following process can be conveniently applied.

To two grams of the powdered alloy add 45 c.c. 1.20 nitric acid, and 25 to 30 drops of hydrofluoric acid. When, without the application of heat, the reaction subsides, add another 25 to 30 drops; the small portion of alloy then undecomposed goes on boiling. After complete decomposition add permanganate, clear the manganic oxide precipitate with a solution of ferrous sulphate, filter off the graphite, add 6 or 8 c.c. strong ammonium hydrate, precipitate with the molybdate reagent, and weigh finally as lead molybdate according to the more detailed instructions given for steels.

Commercial hydrofluoric acid may contain small amounts of phosphoric acid. It is estimated (and allowed for) by evaporating 100 or 200 drops of the acid with sulphuric acid in a platinum dish until

fumes of sulphur trioxide are given off, transferring to a glass vessel, oxidizing with permanganate, clearing with ferrous sulphate, adding ammonia to precipitation of the iron, re-dissolving in nitric acid, precipitating with the molybdate mixture, and finishing as usual.

### HIGH-GRADE FERRO-SILICONS.

The recently introduced high-grade alloys are quite different materials from the 10-15 per cent. alloys for which the foregoing methods of analysis were designed; it is necessary therefore to note a few of the added difficulties and differences.

#### Carbon.

The carbon is almost wholly in the graphitic state unless the manganese is considerable in amount, but in addition, a portion may also be combined with the silicon in the form of carborundum. As this substance is not decomposed by simple ignition, it is necessary to repeat the combustion with the addition of copper oxide or lead chromate. As an alternative, one or other, or a mixture of both of these reagents may be used in the first instance. The reaction when red lead was used with an 85 per cent. alloy was so violent as to shatter the porcelain boat.

#### Silicon.

The alloys become less and less readily attackable by acids, but more and more so by caustic alkalis, as the percentage of silicon increases. For such as contain less than 30 per cent. of silicon, the process already given for low grade alloys will suffice if it be carried out somewhat differently.

To one gram of the agate-ground material add 50 c.c. of hydrochloric acid and allow to digest, with occasional additions of a few drops of nitric acid. At no time must the liquid be allowed to boil, the object of the heating being to promote the decomposition without seriously weakening the acid. After standing for a few hours in a warm place, the sample should be completely decomposed, the colour having changed from metallic grey to pale yellow. Boil down to one-half the bulk, dilute, filter, etc., as before. The filtrate on re-evaporation will be found to yield from three to five milligrams only of silica. After treatment of the ignited silica with hydrofluoric acid followed by strong ignition, a small grey metallic-looking residue may occasionally

be seen. By digesting with hydrochloric acid, filtering through a small paper, and re-igniting, it may be estimated unchanged as carborundum ( $\text{SiC}$ ).

According to Gray (*Journ. Soc. Chem. Ind.*, 1901), these alloys are decomposed by ignition with Stead's tribasic mixture (p. 134), or by fusion with alkaline carbonates, in which case the carborundum is also decomposed and not in any way observable. The fact that a new platinum dish was perforated in three places by fusing an 85 per cent. alloy with sodium carbonate only, shows that the process has disadvantages. For such alloys as are not decomposed by treatment with nitro-hydrochloric acid, the following method is more satisfactory in many ways.

Place 1 gram of the alloy in a nickel dish which holds at least 100 c.c., and add 7 or 8 grams of pure caustic soda along with 50 c.c. water. Heat gently so that the reaction proceeds at a safe rate, and when the reaction slackens, allow the solution to evaporate to dryness, or nearly so, by means of such an over-night arrangement as is described for the sulphuric acid evaporation of tungstic oxide solutions (p. 148). Boil up the dried mass with water, transfer to a shallow porcelain dish and acidify with hydrochloric acid. It can then be easily seen whether the decomposition is complete or not. Evaporate with excess of hydrochloric acid, etc., as usual. For absolutely exact purposes, it must be remembered that in the evaporation of alkaline silicate solutions with hydrochloric acid, the whole of the silica is never rendered insoluble by one evaporation; it is customary to re-evaporate the filtrate. The filtrate may be used for estimating the sulphur if the sodium hydrate used is sulphur-free, or if the amount it contains is small and known.

The decomposition of the poorer high-grade alloys is not so completely effected by this aqueous caustic soda treatment. With a 30 per cent. ferro-silicon, such as could be decomposed by the mixed acids, a residue of undecomposed powder is obtained when the aqueous extract of the dried mass is acidified with hydrochloric acid. On pouring off the solution, however, the addition of hydrochloric and nitric acids to this residue effects its decomposition as quickly as 10-15 per cent. alloys are attacked. The nickel dish is only very slightly attacked by the caustic soda.

#### Manganese.

Decompose the alloy with nitro-hydrofluoric acid in a platinum dish, boil to expel a portion of the hydrofluoric acid, and proceed either by

the bismuthate or red lead process as for low-grade alloys. A gravimetric estimation may be made on the sample used for the estimation of calcium and aluminium if desired.

### Phosphorus.

Attack in a platinum dish with hydrofluoric acid and 1.42 nitric acid by adding two grams of the powdered alloy, a little at a time, to the acid mixture; evaporate with sulphuric acid and finish as usual.

### Aluminium and Calcium.

These elements may be estimated by opening out as in the estimation of silicon, and making use only of the filtrate. In order, however, to avoid this lengthy preliminary operation, and because large amounts of material can be more readily dealt with, it is better to proceed as follows with the richer of the high-grade alloys. Decompose two grams of the alloy with nitro-hydrofluoric acid, add a few drops of sulphuric acid to prevent volatilization of aluminium during the subsequent ignition, evaporate to dryness and ignite. Digest with hydrochloric acid, fuse any insoluble residue with sodium carbonate, and after extracting with hydrochloric acid, add to the main solution. This solution now corresponds in all respects to that of an iron ore, and contains iron, aluminium, manganese, calcium, and magnesium. Titanium, if present, would also be in this solution. Add a small excess of ammonia, filter off iron and aluminium hydrates, and estimate the calcium by precipitation as oxalate and ignition to oxide; or to sulphate after treatment with sulphuric acid.<sup>1</sup> The magnesium is determined in the usual manner in the filtrate as pyrophosphate. If the alloy contains manganese, this element must be removed with bromine and ammonia before the estimation of the alkaline earths. If required, the manganese can be estimated after precipitating the iron and aluminium in the first instance with ammonium acetate instead of ammonia. The precipitated hydrates of iron and aluminium are re-dissolved in hydrochloric acid, and the aluminium determined by precipitation with sodium phosphate and sodium thiosulphate, just as in the determination of this element in steel or ferro-aluminium alloys.

<sup>1</sup> Gray has found as much as 14 per cent. of calcium in a high-grade ferro-silicon: the analysis is given on p. 125. The other unusual impurities given in Gray's analyses, such as chromium, nickel, tungsten, etc., are purely accidental, and result from the fact that previous charges of ferro-alloys had not been completely extracted from the electric furnace.

### Titanium.

Titanium occurs very frequently in these alloys, and when associated with aluminium either element interferes with the accurate determination of the other. In the preceding process for the estimation of aluminium, the whole of the titanium (combined with more or less phosphorus pentoxide) is in the aluminium phosphate precipitate. If therefore, on treatment of this precipitate with hydrochloric acid, a clear solution is formed to which the addition of hydrogen peroxide imparts no colour, there is no titanium present. If this element is present, some of it goes into solution and some not, when hydrochloric acid is added to dissolve the aluminium phosphate. The insoluble part is filtered out, any silica eliminated with hydrofluoric and sulphuric acids, the solution obtained added to the one containing the soluble part, and the whole re-precipitated. The ignited phosphate precipitate of alumina and titanic oxide is then crushed to a fine powder with the agate pestle, mixed with 6 to 8 times its bulk of sodium carbonate, and the mass kept in gentle fusion in the muffle for ten minutes. The fusion should be quite liquid, but not needlessly hot, as the results will be too high if the platinum is attacked. Digest the melt with the least possible quantity of water, filter, and wash with hot water containing a small quantity of caustic soda. Acidify the filtrate, and precipitate the aluminium as phosphate. On dissolving the ignited aluminium phosphate in hydrochloric acid, it should give a practically clear solution, and not more than a faint yellow tint on adding hydrogen peroxide. The sodium carbonate and caustic soda used should be tested for alumina. The residue of sodium titanate is ignited, with the addition of a pinch of sodium carbonate, to get rid of the paper, dissolved in hydrochloric acid to a clear solution, and re-precipitated by boiling with sodium thiosulphate as in the estimation of titanium in steels (page 96), in order to bring the titanium into a weighable form, and at the same time eliminate the small quantity of iron which may accompany it. In the absence of iron, the titanium can be more easily handled by adding an excess of ammonia, then acidifying with acetic acid, and igniting the collected precipitate to titanic oxide.

F. A. Gooch, to whom chemists are indebted for the solution of more than a few difficult analytical problems, has devised two processes for the separation of aluminium and titanium, which are based on the facts that (1) "titanium is completely precipitated and aluminium held in solution when an ortho-phosphate, strongly acidified with formic

acid, is added to the solution of the salts of these elements," and (2), "alumina is soluble and titanic hydrate insoluble in sufficiently strong boiling solutions of acetic acid." The first of these two methods, briefly stated, consists in the treatment of the solution containing salts of the elements in question with a mixture of microcosmic salt and formic acid in the proportion of two to three by weight, together with sufficient ammonium formate to 'take up' the strong acids. The precipitate is fused with sodium carbonate, extracted with water, the residue fused again with a small amount of carbonate, dissolved in sulphuric acid and precipitated by ammonia with the subsequent addition of an excess of acetic acid to the boiling solution. The difficulty of filtering the precipitated phosphate is a drawback to the usefulness of this process. The second method involves many different manipulations, viz.: the addition to the solution of the two elements of sufficient acetic acid to make from 7 to 11 per cent. by volume of the absolute acid, together with sufficient sodium acetate to fix all the stronger acids, and then boiling, filtering, washing with acetic acid of 7 per cent. strength, fusing the ignited precipitate with sodium carbonate, dissolving in strong sulphuric acid, pouring into water, neutralizing with ammonium hydrate, re-dissolving the precipitate in sulphuric acid, and precipitating finally by boiling with acetic acid and sodium acetate as at first. The whole process, according to this description, appears to be long and tedious, but the individual operations themselves do not occupy very much time and are not of a difficult character, so that the separation may be effected with ease and a fair degree of rapidity.

### CARBORUNDUM.

Carborundum, or silicon carbide ( $\text{SiC}$ ), has been proposed for use in steel-making instead of ferro-silicon; it is almost quite free from sulphur and phosphorus, scratches the ruby, and has a specific gravity of about 3.2. It is not attacked by melted potassium nitrate or chlorate, nor by boiling sulphuric, hydrochloric, nitric, nitro-hydrochloric, or nitro-hydrofluoric acids. In a state of fine powder, which is not easily secured, even in an agate mortar, it is decomposed by fusion with caustic soda, or with a mixture of caustic soda and potash. Commercial varieties of the material usually contain from 60 to 63 per cent. of silicon, 30 to 35 per cent. of carbon, and 2 to 4 per cent. of iron and aluminium; sometimes charcoal or powdered coal is present, apparently as an adulterant.

The silicon, iron, and aluminium are determined on half a gram of the finely divided material, which is opened out by prolonged fusion with caustic alkalies in a capacious crucible. Evaporation of a hydrochloric acid extract yields the silica, in the filtrate from which the iron and aluminium are determined, as in the analysis of a refractory material.

Only a small portion of the carbon, other than that due to admixed charcoal or other carbonaceous matter, is burned off by igniting the sample alone in a stream of air. Moissan states that repeated treatment with fused lead chromate is necessary to obtain complete combustion of the carbon; we have, however, experienced no difficulty in obtaining perfect combustion when the sample is ignited with 8 or 10 times its weight of red lead.

TYPICAL ANALYSES.

	Ferro-Silicons.				Silico-Spiegels.	
Carbon, - - -	0·52	0·52	1·03	1·54	2·00	1·70
Silicon, - - -	44·05	83·27	68·65	13·30	13·49	10·50
Manganese, - - -	3·51	0·40	0·20	3·99	20·64	18·34
Sulphur, - - -	0·045	0·05	0·014	0·030	0·047	0·066
Phosphorus, - - -	0·013	0·05	0·034	0·057	0·136	0·098
Iron, - - -	45·28	12·28	9·91			
Aluminium, - - -	0·47	1·66	2·40			
Calcium, - - -	3·29	0·20	14·40			
Magnesium, - - -	0·44	traces	0·31			
Titanium, - - -	0·00	0·51	—			
Tungsten, - - -	0·42	—	0·18			
Chromium, - - -	1·62	—	3·01			
Copper and Nickel, -	traces	—	0·01			
	99·658	98·94	100·148			

MANGANESE ALLOYS.

SPIEGEL AND FERRO-MANGANESE.

Carbon.

As these alloys are decomposed by copper solutions the process given for steels on p. 13 is available. Powdered spiegels may be ignited alone in a stream of oxygen with almost perfect results. But ferro-manganese is not nearly decarbonized by simple ignition, although it is not



refractory in the same way as ferro-chromium alloys are : a hard fritted surface forms, which may prevent easy contact of oxygen and metal. By igniting powdered spiegel or ferro-manganese with zinc oxide all the carbon passes off as dioxide. Oxide of zinc is preferable to copper oxide or lead chromate in this case, because it is quite free from blank after ignition, and any of the oxide reduced to metal by manganese is so readily re-oxidized that no metallic beads can vitiate the assay.

### **Manganese :**

#### **Separation of Iron and Titration with Permanganate.**

Dissolve one to one and a half grams of the powdered alloy, and make an acetate separation of the iron as is described for estimating manganese in steels, page 30. If the neutralization be carried too far by the use of ammonia, the precipitated and readily-oxidized hydrate of manganese is not easily re-dissolved by a few drops of hydrochloric acid. Ammonium carbonate, therefore, should be used to finish the neutralization with, so that this difficulty may be avoided.

Certain corrections must be made when an aliquot part of a hot solution is used for the assay of a high percentage alloy. If the total volume is a litre, and half a litre of the clear solution is filtered off, it should be corrected for : (1) Half the volume of the precipitate ; (2) contraction due to fall of temperature between the two measurings ; and (3) a slight correction due to evaporation whilst filtering.

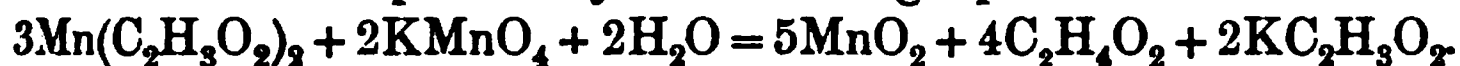
For spiegel or ferro-manganese the correction for bulk of precipitate is less than half a c.c., and may be neglected. The second correction can be made from the table on page 31, although under uniform conditions of working the observed temperature varies not more than 2° C., and a constant correction can be adopted. The third correction depends on form of vessel used, rapidity of filtration, and other incidents. But by precipitating in a flask marked at about 1000 c.c., transferring to a litre flask with a graduated neck, allowing the precipitate to subside, and measuring off 500 c.c. through a syphon filter (page 339), a correction of 1 c.c. should be ample. The filtered fraction may be precipitated with bromine and ammonia, or titrated with permanganate.

The permanganate titration is very accurate, and as it is not interfered with by flocks of basic ferric acetate, an aliquot portion needs decanting merely : it is better, however, to have the previous neutralization and separation made with sodium carbonate and acetate instead of ammonium compounds. The filtered fraction should contain a little free acetic acid, as it will if the acetate separation has been properly made.



Pour the solution of manganous acetate into a constantly-rotated flask, containing an excess of decinormal permanganate and 10 c.c. zinc sulphate solution (200 grams per litre). Allow the precipitate to settle a minute or so, filter an aliquot part through asbestos, acidify, and estimate the excess of permanganate with ferrous sulphate.

The reaction is expressed by the following equation :



Whence each c.c. of decinormal permanganate corresponds to 0.00165 gram of manganese. The permanganate may also be standardized by a spiegel of known composition, or by a pure manganese salt.

The percentage of manganese in speigels is generally known approximately. Failing this, the use of too great an excess of permanganate may be avoided by syphoning off an additional 250 c.c., and adding permanganate to the hot solution until the colour of the supernatant solution is pink. This (Guyard's process) gives a very approximate result.

#### Indirect Volumetric Process.

Riley appears to have originated the indirect determination of manganese by dissolving the alloy in dilute sulphuric acid, titrating the iron, making an allowance for impurities, and obtaining the percentage of manganese by difference. He recognized that the results were subject to variations owing to the presence of soluble organic matter.

Ledebur suggested that the allowance for impurities should be

7.5	per cent.	if the iron is less than 20 per cent.
6.5	„	„ from 20 to 45 „
6.0	„	„ „ 45 to 65 per cent., and
5.5	„	„ „ 65 per cent. or over.

The process usually gives results within a half per cent. of the truth, but occasionally it fails to give results nearer than two or three per cent. The following process, though not quite so rapid, is incomparably more accurate.

#### Bismuthate Process.

Dissolve 1.1 grams of spiegel or 0.275 grams of ferro-manganese in 50 c.c. nitric acid, destroy organic matter by adding bismuthate and boiling, and then dilute the cooled solution to 100 c.c. Mix 25 c.c. of the manganese solution with 30 c.c. 1.20 nitric acid, add an excess of bismuthate, shake well, and filter through asbestos. Dilute the filtrate with an equal bulk of water, add ferrous ammonium

sulphate, and titrate the excess with decinormal permanganate solution exactly as in the determination of manganese in steel.

The filter always retains a little permanganate, but its amount when the washings are colourless is almost insignificant. By boiling the filter and excess of bismuthate with nitric acid and a little sodium peroxide, cooling, and re-oxidizing, we have never found more manganese than is equivalent to 0.2 c.c. decinormal permanganate if the operation has been properly performed in the first instance. Manganese dioxide is always filtered off with the excess of bismuthate unless the oxidation is made as above in very acid solutions.

### **Sulphur and Silicon.**

These elements are determined as in steel.

### **Phosphorus.**

As in steels. More permanganate is needed to produce a permanent precipitate of manganese dioxide on account of the large amounts of combined carbon these alloys contain. A portion of the organic matter in ferro-manganese solutions is not destroyed, and should be filtered off, otherwise the ammoniacal solution of phospho-molybdate, and the precipitated lead molybdate may have a brown colour. The accuracy of the results is not interfered with even if the unoxidized organic matter is not filtered off.

The crystalline needles seen on the surface of ferro-manganese generally contain much less phosphorus than the mother metal, *e.g.* crystals 0.047, and metal 0.24 per cent. phosphorus.

### **Copper.**

This element is invariably present in small amounts; estimate as in steel.

### **Titanium.**

Mr. T. W. Hogg says that there are about half a million isolated crystals of cyano-nitride of titanium in each cubic inch of the high percentage ferro-manganese alloys used for steel making; titanium nitride and carbide being also occasionally present. The size of these crystals generally lies between one ten-thousandth and one thousandth part of an inch; they occur in the form of cubes, octahedra, and forms resembling the icosatetrahedron, which possess a metallic lustre, and have mirror-like facets.

The crystals are separated from ferro-manganese by careful elutriation of the carbonaceous residue left on treating considerable quantities

of material with hydrochloric acid, copper chloride solution, or dilute nitric acid. The last reagent is most convenient. In using it the mixture is kept as cold as possible, and allowed to stand for twenty-four hours. The large crystals separate at once, the small ones being retained in the residue, which must be dried and gently pounded before submitting it to elutriation. The elutriation is performed in a large porcelain basin, using plenty of water, and gently rocking and rotating the mixture, and allowing it to rest at intervals ; the lighter portions are thus separated until nothing but the copper-coloured crystals are left.

The presence of titanium is easily detected and its amount determined by fusing the carbonaceous residue with potassium bisulphate and adding hydrogen peroxide to the cold acidified solution of the melt. If hot nitric acid is used for the decomposition any titanium carbide would, of course, be dissolved, but with either hydrochloric acid or copper solution it remains unattacked.

TYPICAL ANALYSES.

	Ferro-Manganese.		Spiegels.	
Carbon, - - - -	6.52	6.64	4.47	5.35
Silicon, - - - -	1.77	0.61	0.81	0.93
Manganese, - - -	82.30	80.10	9.90	23.15
Sulphur, - - - -	0.006	0.01	0.005	0.036
Phosphorus, - - -	0.128	0.083	0.057	0.067
Copper, - - - -	0.137	0.254	0.085	—
Titanium, - - - -	—	0.16	—	—

CHROMIUM ALLOYS.

FERRO-CHROMIUM.

Carbon.

Direct combustion of the powdered alloy with an oxidizing reagent is the simplest and most accurate method for determination of the carbon in these very refractory alloys. The general procedure for direct combustion is given on p. 6 *et seq.*

We have ignited powdered ferro-chromium with most of the reagents

which have at any time been suggested; the preference must certainly be given, for reasons already stated, to red lead or lead peroxide, whichever is obtainable with the least blank. If a very hot furnace is available, the combustion may also be completed when lead chromate, cupric oxide, or stannic oxide is used. More recently<sup>1</sup> we have used the sesquioxide of bismuth with very good results. After ignition in the muffle to incipient fusion, grinding and sieving, this latter reagent gives no blank and absorbs no carbon dioxide from the atmosphere: in these respects it is superior to any of the oxides of lead.

#### Silicon.

The following process was devised by Dr. Tate. Fuse two grams of the powdered alloy with five times its weight of sodium peroxide in a nickel crucible. The fusion is dissolved in water, transferred to a capacious nickel dish, treated with hydrochloric acid short of actual acidity and evaporated to dryness. The residue is broken up, 40 c.c. of strong sulphuric acid poured on and heat applied until the sulphuric acid begins to fume. By this means hydrochloric and chlorochromic acid are volatilized and the silica dehydrated. The sulphuric acid solution is cooled, diluted, transferred to a porcelain dish, and boiled until the sulphates have dissolved. The silica is then collected, ignited, and weighed.

About 90 per cent. of the chromium can be volatilized in the above manner, and although this removal tends to prevent contamination of the silica by basic salts of chromium, the real silica is in all cases best determined by loss in weight after evaporation with hydrofluoric and sulphuric acids followed by strong ignition. A blank test should be made of the reagents.

The silicon may also be estimated as silica is in chromite on p. 208.

#### Manganese.

Fuse 1.1 grams of the powdered alloy as for silicon, dissolve the melt in water, boil for a few minutes, and filter off the peroxides of iron, manganese, and nickel. As the mixed peroxides filter badly but settle readily, they should be boiled repeatedly with water containing a little ammonium carbonate, and not collected on the asbestos filter until the yellow chromate colour is barely or not at all visible in the washings. The residue and filter are then returned to the beaker, 30 c.c. of 1.20 nitric acid, and as much sulphurous acid or hydrogen peroxide solution added as is needed to completely reduce and dissolve

<sup>1</sup> Midsummer, 1900.

the higher oxides of manganese and nickel. The solution is then made quite cold and, without filtering off the asbestos, oxidized with bismuthate and titrated with ferrous sulphate and permanganate as on p. 34.

The titrated solution has a green colour due to nickel derived from the crucible. A small excess of permanganate makes this green solution quite colourless. The nickel of the crucible is usually quite free from manganese.

### Sulphur and Phosphorus.

A method for determining the approximate amounts of sulphur and phosphorus depends on the assumption that these elements go into solution when the powdered material is boiled with aqua regia, although of course the alloy is by no means completely decomposed.<sup>1</sup> The scientific value of such procedures is not very great, but as approximate results will often suffice, and as the means of making the estimation are always at hand and ready for use, they have a very considerable practical value.

Arnold's instructions for determining either sulphur or phosphorus are: Boil 3.6 grams of the alloy which has passed through a ninety-mesh sieve with 100 c.c. aqua regia.<sup>2</sup> The solution is boiled to low bulk in a covered beaker and then gently evaporated to dryness. The dry mass when cool is taken up in hydrochloric acid, re-evaporated to low bulk, made up to 60 c.c. and 50 c.c. (equal to three grams of the alloy), filtered off and precipitated with barium chloride. The aqua regia solution need not be evaporated beyond low bulk for the phosphorus estimation. Filter the solution as before, and add successively excesses of ammonia and nitric acid, and finally the molybdate reagent. The precipitated phospho-molybdate may be dealt with as usual.

Sulphur and phosphorus may both be estimated on the same sample in the following way, which leaves less uncertainty in the mind regarding the accuracy of the results, though they are still not altogether above suspicion. Mix two grams of the powdered alloy with fifteen grams of tribasic reagent (p. 134), and heat for two hours in the muffle; or open out as for silicon with sodium peroxide over a spirit

<sup>1</sup> Alloys containing sixty or seventy per cent. chromium which contain very little carbon—*e.g.* one per cent. or less—are readily decomposed by boiling with dilute sulphuric or hydrochloric acid, and may then be analysed like chromium metal.

<sup>2</sup> Made by mixing four volumes of strong hydrochloric acid with one volume of 1.42 nitric acid.

lamp. Digest the oxidized mass with water and dissolve to a clear solution with hydrochloric acid. Then add a small excess of ammonia and filter off the precipitated basic phosphate and chromate of iron.

The sulphur is in the filtrate, and, after adding a small excess of hydrochloric acid, may be precipitated with barium chloride as usual. The ignited barium sulphate may contain a small amount of chromic oxide, whether the precipitation was made from an acidified solution of chromic chloride or of sodium chromate.

The residue which contains the phosphorus is dissolved in dilute nitric acid, the little chromic acid present reduced by a few drops of sulphurous acid, ammonia added to neutralize the free acid, and then 30 c.c. of the nitro-molybdate reagent. The precipitated phosphomolybdate is transformed to lead molybdate as usual.

The sodium peroxide or tribasic reagent used in the above operations should be as free from sulphur and phosphorus as possible. The magnesia or lime for the latter is best prepared from the carbonate by heating at a high temperature and then powdering. In any case it is necessary to make a careful examination of the reagents.

### Chromium.

Oxidation of the powdered alloy by fusion with sodium peroxide is the most expeditious preliminary either for volumetric or gravimetric estimations of chromium. All technical analyses are made by the volumetric process, that form of the titration which is the inverse of the bichromate estimation of iron being generally employed. The precautions named on p. 109 *et seq.* are equally important in relation to the estimation of chromium. Neglect of these is generally the cause of such trade disputes as are not directly due to imperfect sampling or the use of different atomic weights.

### Peroxide Method.

From a half to one gram of the finely powdered and agate-ground <sup>1</sup> ferro-chromium is mixed with five times its weight of sodium peroxide, and heated gently over a bunsen flame in a nickel crucible until the mixture begins to soften and then glows spontaneously. The mass is kept just liquid and in constant rotation for a few minutes, and then allowed to cool. Clean off any sooty deposits, which form with great facility on nickel even in non-smoky flames, and add water to the

<sup>1</sup> A little water may be added to facilitate grinding (Rideal and Rosenblum), but most rich ferro-chromium alloys are decomposed completely if they have passed a sieve of ninety meshes to the lineal inch.

melt, keeping the crucible covered as much as possible so as to avoid loss. The solution is then transferred to a beaker or flask and diluted.

From this point either of two ways may be adopted according as manganese is being determined or not. If it is, boil the solution for five or ten minutes to decompose sodium ferrate and manganate and any excess of sodium peroxide, and filter off the insoluble residue. After washing quite free from sodium chromate the residue is used for the determination of manganese in the above-described manner. The filtrate is cooled, acidified with sulphuric acid, and titrated with permanganate, or bichromate and ferri-cyanide, in the usual way.

If the estimation of manganese is not contemplated, then the boiled alkaline solution may be acidified, a small excess of permanganate added to safeguard the reduction of any chromic acid by small amounts of hydrogen peroxide which were not eliminated from the alkaline solution, and then enough dilute hydrochloric acid to destroy the excess of permanganate as is done in Stead's modification of Galbraith's method for estimating chromium in steel. After boiling off chlorine the solution is cooled and titrated with ferrous sulphate and bichromate.

One objection to the peroxide process is that vessels of all kinds—platinum, gold, silver, nickel, etc.—in which the decomposition is made are destructively attacked. Nickel crucibles are most used on account of their cheapness, but even when care is taken to avoid needlessly high temperatures they lose from one to two decigrams at each fusion.

Nickel, like manganese, unless care is taken, may interfere with the titration by masking the colour of the ferri-cyanide indicator, and on this account some analysts *insist* on the insoluble peroxides being filtered from the alkaline solution in order that a sharp end reaction, on which so much depends, may always be secured.

This last consideration should be kept in mind whenever iron is being estimated. This is done of course by dissolving the insoluble oxide in hydrochloric acid, reducing and titrating. If the volume of liquid is comparatively small the nickel it contains has a very obvious effect on the ferri-cyanide indicator. If the peroxides are dissolved in dilute sulphuric acid assisted by a little sulphurous acid, and then reduced and titrated with permanganate, the presence of nickel does not interfere.

#### **Tribasic Method.**

Instead of the common fusion mixture of caustic soda and some infusible oxide like magnesia to keep the mass open and promote

oxidation, the following tribasic mixture, which has the advantage of not attacking platinum, has been suggested by Stead :

Lime or Magnesia, -	-	-	-	200 parts.
Sodium Carbonate, -	-	-	-	50 parts.
Potassium Carbonate, -	-	-	-	50 parts.

From a half to one gram of the floured alloy is mixed with ten times its weight of this mixture and heated at bright redness in the muffle for from one to two hours. The dish containing the sintered mass is placed in a capacious beaker, about 300 c.c. water and 30 c.c. strong sulphuric acid added, and the whole heated until everything passes into solution. After cooling add ferrous sulphate and titrate as usual.

Mr. Stead found that the oxidation of both alloys and ores was complete in about an hour. He gives the following figures obtained by heating the mixture for varying periods of time :

Time Heating.	Cr in FeCr.	Cr in Ore.
5 minutes, - -	60.62 or 97.6 per cent.	30.70 or 89.0 per cent.
60 minutes, - -	61.94 or 99.9 „	34.50 or 100.0 „
120 minutes, - -	61.99 or 100.0 „	34.49 or 100.0 „

If a portion of the alloy is undecomposed the assay should be repeated with more finely ground material or by heating for a longer time. If very small particles only had escaped oxidation they might dissolve in the acid solution unobserved during the period of effervescence, and therefore the further operation of boiling with a small excess of permanganate and destroying that in turn with a small excess of hydrochloric acid seems a desirable precaution.

## METALLIC CHROMIUM.

### Carbon.

One gram of the powdered metal is ignited with six grams of red-lead as in the determination of carbon in ferro-chromium. But as the carbon is not generally more than a few tenths per cent. and the material is very refractory, it is desirable to effect the combustion at as high a temperature as possible, and to utilize the heat of the reaction to the full extent by putting the boat straight into the hot tube. This cannot be safely done with high-carbon ferro-chromium alloys on account of the violent evolution of gas which would ensue.



### Silicon.

This element may be determined as in steels by dissolving in hydrochloric acid, evaporating to dryness, etc.; it is necessary to treat the siliceous residue with hydrofluoric acid.

### Manganese and Phosphorus.

These elements are determined as in ferro-chromium.

### Sulphur.

As the metal is soluble in dilute acids, any form of the evolution process may be applied, and indeed would preferably be applied even by those who do not regularly use it. On many extempore occasions we have used the simple form of apparatus, shown in Fig. 11, in the following manner.

One or two grams of the finely crushed sample is weighed into the first flask, 30 c.c. strong hydrochloric acid mixed with 30 c.c. hot water added, the stopper quickly replaced and the solution boiled

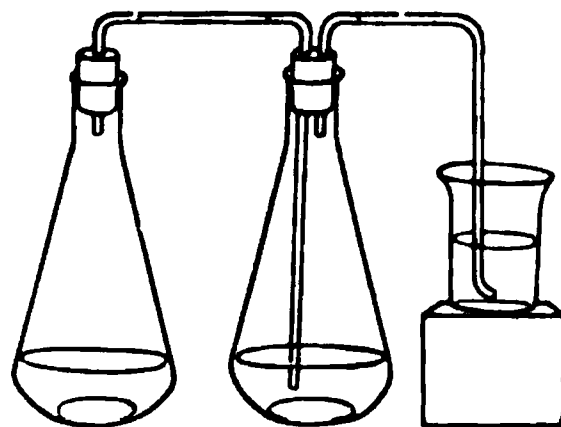


FIG. 11.

until the sample is dissolved. The second flask contains a faintly acetic solution of lead acetate, and the beaker contains a similar solution, but its only purpose is to indicate any imperfect absorption by the first solution.

When the sample is dissolved and all the sulphuretted hydrogen has been driven from the evolution flask, the precipitated lead sulphide formed in the absorption flask (and in the beaker also if there should be any) is collected on a small pulp filter, washed with hot water, and precipitate and filter digested with 1·20 nitric acid. The paper is strained off by means of a filter plate, the solution of lead nitrate nearly neutralized with ammonia and the remaining free mineral acid destroyed with ammonium acetate. Then one or two grams of ammonium chloride are added and the lead precipitated with ammonium molybdate and subsequently ignited and weighed as lead molybdate. The weight of the lead molybdate multiplied by 0·0872 gives its equivalent weight of sulphur.

### Chromium.

Half a gram of the metal, which need not be very finely powdered, is boiled with 100 c.c. dilute sulphuric acid (1 to 3). When nearly everything has dissolved, as much strong permanganate solution is added as converts most of the chromium to chromic acid, but forms no

precipitate of manganese dioxide: this completely decomposes the remaining particles of carbide. The solution is then cooled and made up to 250 c.c.

Two portions of 100 c.c. each are measured into flasks, diluted to about 300 c.c., 10 to 20 c.c. more dilute sulphuric acid added, and as much permanganate as is necessary to complete the oxidation of the chromium and 10 c.c. in excess. After five or ten minutes' boiling add 30 c.c. strong hydrochloric acid diluted with an equal volume of hot water and boil until the solution clears and the evolved chlorine is driven off; then cool and titrate in the usual way.

When a precipitate of manganese dioxide is destroyed in strong chromic acid solutions particular care should be taken that the hydrochloric acid reduces none of the latter also. When the solution clears the flask should be shaken over a strong flame and the issuing vapours tested with iodized starch paper. In a minute, or even less with vigorous shaking, the dissolved chlorine will have boiled out. If, however, chromic acid is being reduced chlorine will be slowly evolved, and starch paper coloured, for an indefinite time.

The mean of the two results if they agree closely should be taken.

### Iron.

The pure metal is very readily attacked by sodium peroxide. After fusion the acidified solution is precipitated with ammonia and filtered. The residue is re-dissolved in acid, reduced, and titrated with either permanganate or bichromate.

### TYPICAL ANALYSES.

Chromium, - -	97.12	71.00	62.50	64.75	64.00
Carbon, - - -	0.27	1.82	9.54	4.96	2.77
Silicon, - - -	0.75	trace	1.51	0.37	0.12
Manganese, - -	0.11	0.17	0.16	0.13	0.10
Sulphur, - - -	0.18	0.12	0.032	0.087	0.053
Phosphorus, - -	—	0.06	0.034	0.033	0.011
Aluminium, - -	—	—	2.83	0.30	0.15
Magnesium, - -	—	—	—	0.18	0.15
Iron, - - -	1.50	26.24	23.25	29.07	32.55
	99.93	99.41	99.856	99.88	99.904

The analyses showing aluminium and magnesium were kindly communicated by Mr. G. Watson Gray.

## NICKEL ALLOYS.

### THE CYANOMETRIC ESTIMATION OF NICKEL.

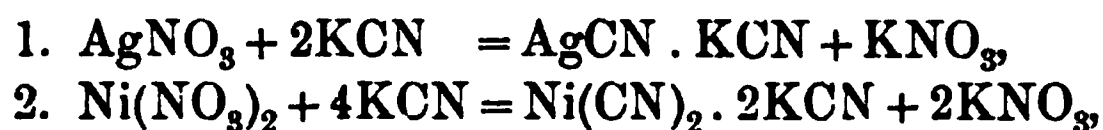
The cyanometric estimation of nickel is particularly adapted to the analysis of alloys, because there are so few metals at any time alloyed with nickel which interfere with the titration or whose interference may not be obviated by some trifling modification of the process. After some particulars concerning the solution to be titrated, the indicator, the potassium cyanide, and so on, the behaviour of the process in the presence of various elements will be observed. It is hoped that in this way provision may be made for assaying nickel in any combination of elements likely to come into the steel works' laboratory, and also to some extent for the alloys of nickel so extensively used in the lighter trades of Sheffield, Birmingham, etc.

**The Solution to be Titrated.**—This must be alkaline. A large excess of ammonia must be avoided not merely because it increases the solubility of the silver iodide indicator, but because it interferes with the formation of the double nickel-potassium cyanide. A solution containing two per cent. of its volume of binormal ammonium hydrate titrates perfectly, and several times that amount are not harmful. It is occasionally advantageous to make alkaline with sodium or ammonium carbonate. (See titration in the presence of zinc and uranium, p. 141.)

**The Silver Iodide Indicator.**—The intensity of the cloud formed on adding silver nitrate to the alkaline solution containing potassium iodide is increased by the presence of alkaline salts. Sulphates are most effective, then nitrates, then chlorides. This explains why ammonium sulphate is always added before the silver nitrate. The indicator is the more sensitive the less potassium iodide there is used in excess of that needed to form the working turbidity with the silver nitrate. The depth of turbidity is a matter of taste, but the addition of two cubic centimetres of a two per cent. potassium iodide solution for each five hundred cubic centimetres of solution titrated provides the deepest desirable cloudiness.

**The Potassium Cyanide.**—Neutral solutions of potassium cyanide should not be needlessly exposed to the air because they absorb carbon-dioxide and give off hydrocyanic acid: hence the characteristic smell. In well stoppered bottles, however, such solutions suffer no appreciable change during two or three weeks, and when containing a small excess

of caustic soda the solutions are practically permanent. The cyanide solution may be standardized with some well-defined nickel compound, as pointed out on page 72, or with silver nitrate or pure silver trial plate, and the nickel equivalent calculated from the following equations :



whence  $\text{Ag} \times .272 = \text{Ni}$ . The results of each method of standardizing are in perfect agreement.

Thomas Moore has described a modified form of the titration depending on the following: "When a solution of potassium cyanide containing a small quantity of argentic cyanide is added to an ammoniacal solution of nickel containing potassic iodide, it is seen that argentic iodide is precipitated, and the turbidity thus formed in the solution continues to increase up to the point where the formation of the nickelo-potassic cyanide is complete; any further addition, after this stage is reached, will produce a clearing up of the liquid until at last the addition of a single drop causes the precipitate to vanish. This final disappearance is most distinct and leaves no room for doubt."

### THE TITRATION.

The solution titrated must be cold. When a number of samples has to be titrated there is some advantage in adding potassium cyanide with some levity until the solution clears, then going back with silver nitrate and clearing finally with not more than a drop of the cyanide. A further reason for adding the cyanide without undue delay lies in the fact that when only a fraction of the potassium cyanide needed to form the double cyanide of nickel and potassium is added and the solution allowed to stand for a minute, a silky crystalline precipitate forms and carries down the uncombined nickel in a form which is less readily acted upon by a small excess of cyanide. This reaction does not take place in the presence of ammonium sulphate, or rather it proceeds so slowly that no account need be taken of it. The ammonium sulphate added to heighten the silver iodide turbidity is sufficient in amount.

**The Titration in the presence of other Elements.**—The results tabulated were obtained by titrating one decigram of nickel with 0.05 and 0.10 grams of the elements, whose interference was being observed,

in the ordinary manner, except that where the element was precipitated in the alkaline solution, it was filtered off *after* enough cyanide had been added to combine with the nickel present.

Metal.	Nickel Found.		Per cent. Error.
	0·05 grams.	0·10 grams.	
Calcium, - - - -	0·1000	0·1000	0·0
Barium, - - - -	0·0999	—	0·1
Strontium, - - - -	0·1000	0·1002	0·2
Magnesium, - - - -	0·1000	0·1002	0·2
Zinc, - - - -	0·1015	0·1021	2·1
Cadmium, - - - -	0·1002	0·1003	0·3
Aluminium, - - - -	0·0970	0·0956	4·4
Iron, - - - -	0·0989	0·0984	1·6
Manganese, - - - -	0·0999	0·1002	0·2
Chromium, - - - -	0·0888	0·0834	16·6
Tin, - - - -	—	0·1001	0·1
Molybdenum, - - - -	0·1000	0·0999	0·1
Arsenic, - - - -	0·1000	0·1000	0·0
Antimony, - - - -	0·1000	0·1000	0·0
Bismuth, - - - -	0·1002	0·1001	0·1
Lead, - - - -	0·1000	0·0999	0·1
Uranium, - - - -	0·1002	0·1001	0·1
Tungsten, - - - -	0·0999	0·1000	0·0

Moderate amounts of free alkali, alkaline carbonates, chlorides, bromides, phosphates, etc., and salts of the alkaline earths exert no appreciable influence on the results. In the presence of those elements (barium, etc.) which form insoluble sulphates, it is advisable to replace the ammonium sulphate, used to deepen the turbidity, by a chloride or a nitrate.

The only elements which falsify the results to an appreciable extent are zinc, iron, aluminium, and chromium, but the behaviour of some others calls for comment. They are :

**Manganese.**—This element is slowly precipitated in ammoniacal solution, and so it is impossible to take full advantage of the delicacy of the indicator even by repeated filtrations, but the precipitate does not interfere in any other way. The manganese may be kept in solution, and interference of any kind avoided by adding ammonium chloride ; it may also be precipitated from the solution by using ammonium carbonate instead of ammonium hydrate. The manganese carbonate becomes bath-brick coloured and less bulky in form after adding the cyanide, so that it may be readily filtered off. The harmlessness of manganese should be emphasised, because it has been

repeatedly said to render the cyanometric estimation of nickel valueless.

**Tin.**—In the presence of stannous salts a red coloration is produced on adding the cyanide—probably due to a sub-cyanide of nickel. This complication should be avoided by oxidizing the stannous to stannic salts, in the presence of which perfectly accurate estimations can be made.

**Molybdenum.**—The results are liable to error through the precipitation of nickel in the ammoniacal solution in a form not readily acted upon by the potassium cyanide. This nickel-molybdenum precipitate forms only very slowly, and is still further retarded by the presence of ammonium sulphate. If the titration is not unduly delayed after making the solution alkaline the results are accurate.

**Arsenic.**—Compounds of arsenious oxide cause the result to be very slightly low. After converting to arsenates by making slightly acid with nitric acid, adding a little bromine water, boiling off excess and titrating as usual, the results are perfectly accurate. As with molybdenum, there should be no delay between making alkaline and adding the cyanide.

**Antimony and Bismuth.**—The oxy-chlorides formed on diluting do not interfere. By adding a small amount of tartaric acid the direct titration may be employed in the presence of antimony.

**Lead.**—The formation of lead sulphate may be obviated by using ammonium nitrate instead of ammonium sulphate.

**Uranium.**—The precipitate thrown down by ammonia is difficult to filter. Ammonium carbonate is used; an excess re-dissolves the yellow precipitate.

**Iron, Aluminium, and Chromium.**—By adding an excess of cyanide to the ammoniacal liquid in which these metals have been precipitated, filtering off an aliquot part of the clear liquid, and going back with silver nitrate, the results are always low. This is due to much of the nickel being carried down in a form which does not permit it to act so readily with the excess of potassium cyanide. It is remarkable that this error is proportionally such as is found when an attempt is made to separate these metals from nickel by precipitating with ammonium hydrate. For instance, to the solution of a decigram of nickel along with the same amount respectively of iron, aluminium, and chromium, there were added equal amounts of ammonium hydrate. In the appended table is seen how much of this nickel was carried down by the respective hydroxides, and how great an error under like

circumstances the same metal introduces when the cyanometric estimation is carried out in the manner just indicated :

Interfering Metal.	Per cent. of Nickel carried down by the Hydroxides.	Per cent. Error of Potassium Cyanide Estimation.
Iron, - - -	64.2	1.6
Aluminium, - -	81.8	4.4
Chromium, - -	95.9	16.6

These errors can be minimized in various ways, but they are eliminated altogether by permitting the double cyanide of nickel and potassium to be formed before the hydroxides are precipitated. This is accomplished by adding the required amount of potassium cyanide to the neutral or faintly acid solution, and at once adding the usual excess of ammonia to the agitated liquid, filtering off an aliquot part, adding ammonium sulphate and potassium iodide, and titrating the excess of potassium cyanide with silver nitrate. The results are very accurate (see p. 73). This modification is referred to as the 'acid titration.'

**Sodium Pyrophosphate.**—Tartaric and citric acids may be used for preventing the precipitation of iron and aluminium in the alkaline solution. The use of the organic acids is preferable to pyrophosphate, but in any case if very large amounts of these substances are present the silver iodide clears up too soon and then re-appears. Tartaric acid works very well when only alumina has to be kept in solution, but neither pyrophosphate nor the organic acids can be satisfactorily used when chromium is present. Chromates do not interfere with the titration.

**Zinc.**—The interference of this element is eliminated by a modified form of the 'acid titration.' After adding the potassium cyanide make alkaline with sodium carbonate instead of ammonium hydrate. The zinc becomes for the most part precipitated as carbonate, and only a small portion passes into solution as cyanide. From this point the procedure is : Filter off the zinc carbonate by means of a small ribbed paper, and to the filtrate add silver nitrate ; it is an easy matter to distinguish between the iodide turbidity and the small amount of zinc carbonate which the silver displaces from its cyanide combination, and so it is practicable to note, by the readiness with which the superstratified iodide turbidity disappears, when the solution contains only a very small amount of free potassium cyanide. At this point re-pass the solution through the filter previously used. This operation gives a

clear solution in which to observe the end reaction, and also incorporates the stronger cyanide solution which was left in the paper and precipitate on the first filtration. With a knowledge of the approximate amount of nickel present the whole process is very easy and very accurate. The normal titration furnishes the required approximation in a few minutes. The interference of very large amounts of cadmium can be eliminated in the same way.

Moore finds that the titration may be performed in the presence of zinc if "to a slightly acid solution there be added an excess of sodic pyrophosphate until the precipitate which at first forms is re-dissolved to a perfectly clear solution." Certainly the use of this reagent does improve the results, but as pyrophosphate alone tends to lower them, and as the tendency of the zinc is in the opposite direction, the betterment on using pyrophosphate is due, partly at least, to compensatory errors.

**Elements to be separated.**—Cobalt, copper, silver, gold, and metals of the platinum group interfere with the cyanometric estimation in a regular manner, and unless the amount of each is known and can be allowed for, they must be separated. Copper is the only one of these metals which occurs in any appreciable amount in steel-making material. It is most conveniently removed by adding an excess of sulphur-dioxide and some potassium thiocyanate to an acetic acid solution. The cuprous thiocyanate is filtered off and can straightway be estimated by a variety of processes (see Bibliography). The filtrate is made ammoniacal and titrated at once; for neither sulphur-dioxide nor potassium thiocyanate interfere unless the latter contains some cyanide, and then the solution must be acidified with nitric acid and boiled before making alkaline and titrating.

### FERRO-NICKEL: MOLYBDENUM NICKEL: TUNGSTEN NICKEL.

Necessary particulars for the analysis of these alloys are given in the sections devoted to the estimation of nickel in steels and the analysis of molybdenum and tungsten alloys respectively.

### CUBE NICKEL

The estimation of carbon, silicon, manganese, sulphur, phosphorus, and copper is carried out as for steels. The small amount of iron



usually present is precipitated from an acid solution of the metal with ammonium hydrate and estimated volumetrically. Small amounts of oxygen and cobalt and traces of zinc, lead, arsenic, antimony, and tin may also be present, but they have no metallurgical significance to the steel maker. Simply passing sulphuretted hydrogen to saturation through a hydrochloric acid solution of the metal will at once show if these elements, excepting zinc, are present in amounts worthy of consideration. A direct determination of nickel with potassium cyanide standardized against pure silver trial plate, or silver nitrate, at once limits the impurities to a known amount.

## TYPICAL ANALYSES.

Nickel, -	-	-	-	99·33	97·87
Carbon, -	-	-	-	0·134	traces
Silicon, -	-	-	-	0·040	0·19
Manganese, -	-	-	-	0·00	—
Sulphur, -	-	-	-	0·008	0·05
Phosphorus, -	-	-	-	0·006	—
Copper, -	-	-	-	0·107	0·10
Iron, -	-	-	-	0·374	0·45
Cobalt, -	-	-	-	—	1·45

## TUNGSTEN ALLOYS.

## FERRO-TUNGSTEN.

## Carbon.

If the alloy contains at least fifty per cent. of tungsten and not more than two or three per cent. of either chromium or nickel, the carbon may be determined by simple ignition in a stream of air or oxygen, and much poorer alloys may be satisfactorily dealt with in the same simple manner at higher temperatures than are available with the average combustion furnace. Very exact results are also obtained with either high or low percentage alloys by igniting two or three grams with five grams of red lead. The sample need not be finer than passes through a thirty-mesh sieve if red lead is being used.

## Manganese.

Both tungsten powders and many of the alloys contain only such an amount of manganese as is incidental to the process of manufacture,

and that is generally less than a half per cent. It may be estimated therefore by a modification of the Red-Lead Process used for steels.

Pour 5 to 10 c.c. hydrofluoric acid over one gram of the powdered alloy in a platinum basin, add a few c.c. nitric acid, and digest until nearly everything is dissolved. Pour the mixture into 50 c.c. of the nitro-sulphuric solution (page 32), oxidize with red lead and titrate with ferrous sulphate as though an ordinary steel were being dealt with. The trustworthiness of the process has been tested by adding 5 and 10 c.c. hydrofluoric acid respectively to a solution of a steel containing exactly 0.5 per cent. manganese; the results obtained were 0.495 and 0.504 per cent. Also, by adding known amounts of manganese to a solution of tungsten powder prepared in the foregoing manner: in five such tests the greatest error was only 0.02 per cent. manganese.

The above process is not suited for those alloys at one time much used for making self-hard steels, and occasionally containing as much as ten per cent. of manganese. Perhaps the chlorate process would be applicable if the hydrofluoric acid were first boiled off: we have, however, no sure ground for assuming that it would work well in the presence of such large amounts of tungsten. Hydrofluoric acid has been used in connection with the chlorate process by both Norris and Ford and Bregowsky, in order to assist the decomposition of siliceous bodies. The latter even maintain that its presence assists the precipitation of the manganese dioxide.

Neither tungsten nor hydrofluoric acid separately interfere with the bismuthate process for estimating manganese; but when they are present together the results are very erratic and altogether unreliable. If it is desired to assay a ferro-tungsten opened out with fluor-nitric acid, the solution should be evaporated after adding sulphuric acid, until it fumes. Some peroxide of manganese has then a tendency to remain with the insoluble tungstic oxide; the solution should therefore be boiled with a little manganese-free ferrous sulphate, or sulphurous acid, before making up to a definite volume with 1.20 nitric acid and filtering off a fraction of clear liquid on which to make the determination. The use of sulphuric acid should be minimized so that it is of not more than normal strength in the solution oxidized by the bismuthate.

The manganese may also be estimated as it is in ferro-chromium, but it is better to give the sample a preliminary roasting in a platinum dish and to make the fusion with sodium carbonate instead of peroxide, a pinch only of the latter being used to destroy any manganate formed.

### Phosphorus.

Pour 10 c.c. nitric acid (1.42) over two grams of the crushed alloy and add hydrofluoric acid, a few c.c. at a time, until it is decomposed; then add 5 c.c. sulphuric acid and evaporate to pastiness, by which time all or nearly all hydrofluoric acid should have disappeared. To the pasty mass add 20-30 c.c. 1.20 nitric acid, boil and filter. To the clear filtrate add ammonia until all free acid is neutralized, i.e. until the yellow solution becomes red on account of dissolved ferric hydrate—then add 30 c.c. molybdate reagent and finish as usual. The phospho-molybdate generally comes down finely divided and more slowly than in steel solutions; it should be allowed to settle in a warm place until the supernatant liquid is clear. Any phosphorus in the hydrofluoric acid must be allowed for (page 119), and the ignited lead molybdate may be dissolved in a small amount of hydrochloric acid and tested for tungstic oxide (page 56) if thought necessary.

The above process was analytically compared with satisfaction against the following, which may be used instead if preferred:

Roast two grams of the alloy, fuse with sodium carbonate, evaporate the dissolved melt with hydrochloric acid, and filter off tungstic oxide. Add a small excess of ammonia to the filtrate, collect the precipitated ferric hydrate which contains all the phosphorus, dissolve it in 30 c.c. 1.20 nitric acid, neutralize the solution with ammonia, add 30 c.c. molybdate reagent, and finish as usual.

### Sulphur and Silicon.

The alkaline filtrate, mentioned in the last paragraph, from the basic ferric phosphate precipitate may be acidified and the sulphur precipitated with barium chloride if the metallic alloy is fused with sodium carbonate without a preliminary roasting. Otherwise heat one gram of the powdered alloy over a spirit lamp with four or five grams of potassium nitrate. Dissolve the melt in water, acidify strongly with hydrochloric acid, and evaporate to dryness. 'Take up' again in hydrochloric acid, evaporate to low bulk, dilute and allow to digest for a time in order to favour the complete separation of tungstic oxide. Then filter and add barium chloride. If the acid solution is allowed to stand for several days the barium sulphate may be mixed with a little tungstic oxide. In such a case the filter, after freeing from iron, should be washed with dilute ammonia until it no longer has a yellow colour, and then again with water before igniting. See Determination of Sulphur in Tungsten Powders, page 152.

If the fusion and subsequent evaporation in the preceding case

have been carefully made, the residue will contain all the tungsten and silicon. After thorough washing with dilute hydrochloric acid, ignite and weigh. Drench the precipitate with hydrofluoric acid, evaporate so as to avoid spurting, and re-ignite. The loss is silica, which is calculated to silicon.

#### **Tungsten.**

It is not desirable to always use one and the same method for the estimation of tungsten in these alloys since variations in the tungsten of from twenty to ninety per cent. cause them to behave differently with any specific reagent; moreover, one has occasionally to think of estimating some other constituent besides tungsten on the same sample. We shall therefore describe several processes and remark on their limitations.

**Method I.**—After the removal of silica with hydrofluoric acid (see Estimation of Silicon) the residue should consist of pure tungstic oxide; almost invariably, however, it contains small amounts of ferric oxide. Fuse therefore with sodium carbonate, dissolve the melt in water, collect the insoluble ferric oxide, ignite, weigh, and deduct its amount from the gross weight of the residue. The difference is calculated to metallic tungsten.

**Method II.**—The powdered alloy is roasted so that as far as possible the carbon may be eliminated and the tungsten oxidized. It is then mixed with four or five times its weight of sodium carbonate with or without a pinch of nitrate and fused: any other fusion mixture may be used. The heating is best done in a muffle, as an even temperature can be more easily maintained than by means of the blow-pipe flame, and the platinum is attacked less. After being kept in the liquid state for fifteen or twenty minutes, the melt is boiled with water and filtered. The filtrate is neutralized by 1.20 nitric acid using methylorange, and then the tungsten precipitated as mercurous tungstate (or possibly a mixture of mercurous tungstate and tungstic oxide) by adding mercurous nitrate in excess and then a small excess of amorphous (yellow) mercuric oxide, which leaves no residue on ignition.

The former reagent may be prepared by mixing 56 grams mercurous nitrate with 40 c.c. 1.20 nitric acid and diluting to a litre with water. The solution is preserved in a stoppered bottle containing also a little metallic mercury. Mercuric oxide may be preserved as a water emulsion, or it may be prepared as required by adding caustic soda short of alkalinity to a solution of mercuric nitrate.

The mercurous tungstate is thoroughly washed, by decantation,

with hot water, collected on the filter, ignited gently until the mercury is volatilized, then more strongly, and weighed. The silicon in the alloy, and probably also a little taken up from the glassware during the operations, is precipitated as mercurous silico-tungstate. After weighing, therefore, the precipitate must be treated with hydrofluoric acid and again ignited and weighed. The residue should be pure tungstic oxide.

This method may be used for alloys of any percentage. Where very much iron is present, or there is any reason to suspect an incomplete transformation to sodium tungstate, the residual ferric oxide is ignited gently to destroy the paper pulp, dissolved in hydrochloric acid, evaporated nearly to dryness and diluted, and any precipitated tungstic oxide recovered.

If the alloy contains aluminium it will be found, at least partly, along with the mercurous tungstate. The suggested means of separating alumina by adding an excess of ammonia to the acidified sodium tungstate solution and filtering off requires supporting by experimental evidence before being relied on; or as a safeguard the moist precipitate should be dissolved in hydrochloric acid and tungstic oxide looked for after evaporation. The presence of chromium in an alloy also interferes with this method; although, if the roasted alloy be fused with sodium carbonate only at the back of the muffle, a portion only of the chromium—and sometimes none—gets oxidized to sodium chromate.

**Method III.**—If one to two grams of the finely agate-ground alloy is treated with 50-100 c.c. hydrochloric acid and a little nitric acid in the manner described for the determination of tungsten in steels on page 77, it will dissolve completely. After evaporating to pastiness, diluting with hydrochloric acid (1 to 4), and boiling, the tungstic oxide is easily filtered and washed. The estimations of tungsten and silicon are concluded as usual. The advantages of this method are:

(1) Chromium, if not more than a few per cents., passes into solution, and so of course does any aluminium that may be present. (2) The filtrate contains all the molybdenum, which may be estimated as in steels.

Ferro alloys containing up to 70 per cent. tungsten can be decomposed in this way, but the material must be in a fine state of division and the hydrochloric acid kept as strong as possible until everything is dissolved.

**Method IV.**—Cover one to two grams of the powdered alloy<sup>1</sup> in a

<sup>1</sup> If a pure ferro-tungsten alloy, very coarse material should be used, so as to moderate the reaction with the mixed acids.

tared platinum dish with hydrofluoric acid and add strong nitric acid, a little at a time, keeping the basin covered as much as possible. When further addition of nitric acid causes no energetic attack of the metal, as may happen with highly chromiferous alloys when a considerable portion is undecomposed, then add 10 to 15 c.c. strong sulphuric acid and allow to digest until decomposition is complete.

The solution may now be treated in a rapid or a slow way. If the result is required without delay, wash the platinum cover and arrange the basin on a sheet of perforated asbestos millboard over a lighted bunsen with a rose burner, so that after a time it would boil briskly if left to itself. Then rotate the basin with one hand, and with the other direct a continually shifting stream of air on to the surface of the liquid so as to prevent the loss which would otherwise occur through the bursting of bubbles. This operation must be continued with increasing vigilance until dense fumes of sulphuric anhydride are given off and the precipitated tungstic oxide, at first white, becomes yellow. When this point is reached—i.e. in five or ten minutes—cool the basin in water, add dilute hydrochloric acid (1 to 5), and boil so as to bring all the iron, (and if present in considerable amounts) manganese, and chromium into solution.

The slower, but more pleasant means of reaching the same stage, is to arrange a basin over a bunsen burner, in some such fashion as is

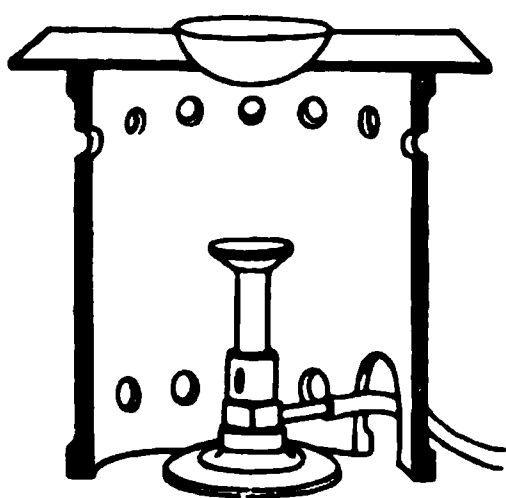


FIG. 12.

suggested by the sketch (Fig. 12), that it may be left evaporating over night. A trial is needed to show the size of flame to be provided, in order to completely drive off the hydrofluoric and nitric acids by the following morning, without causing too great an evaporation of the sulphuric acid. In this way the tungstic oxide separates on the surface and falls to the bottom of the basin in flakes, which are very easily filtered and washed.

After the sulphuric evaporation the dish is covered on the inside by a film of tungstic oxide of rainbow hues, which cannot be removed by rubbing. This film frequently weighs from ten to fifteen milligrams, so that it can by no means be considered a trifle. But if the platinum dish is tared before weighing the powder into it, the film need not be removed, as the dish is not in the least attacked by the operation.<sup>1</sup> Collect the precipitate then on a pulp filter, wash well, and return to the dish and ignite. There is, of course, no silica with the tungstic oxide ;

<sup>1</sup> The acids used should of course be free from chlorides.

there may be, however, and generally is, a little ferric oxide, which must be determined, by fusing with sodium carbonate, etc., and deducted.

The following are results of every-day determinations, made by the methods described, on various alloys :

Method.	Tungsten per cent.				
I., - -	—	75·0	—	69·5	39·0
II., - -	68·6	—	70·9	—	38·9
III., - -	68·3	—	—	69·3	—
IV., - -	—	{74·9 75·2}	70·6	—	38·8

### Chromium.

This element may be incidentally present in ferro-tungstens, but it is often purposely added in large amounts to such alloys as are sold for making self-hard steels.

As before, the alloy is most readily opened out with a hydrofluoric acid mixture. This mixture, however, is objectionable to any of the processes used for the estimation of chromium in steel, chiefly on account of the tendency hydrofluoric acid exhibits to prevent the oxidation of chromium by permanganate. It is possible, unless a large amount of manganous sulphate is in solution, to add a little permanganate to a solution of chromic oxide, and not have it decolourized by vigorous boiling

If much manganous sulphate is present the solution has a clear yellow colour only after a large precipitate of manganese dioxide has been formed. If enough permanganate is added to form only a small precipitate, the solution has a brown colour due to dissolved peroxide, or some more oxygenated compound than  $MnO$ . Since large precipitates carry down some chromic acid, the process known in England as Galbraith's, and those of a like kind, cannot be relied upon under these circumstances. But Stead's modification (page 62), where the precipitated dioxide is purposely made large, and then dissolved in hydrochloric acid, gives satisfactory results if no nitric acid is used.

In order to avoid nitric acid digest the sample with a mixture of sulphuric and hydrofluoric acids, and then add an excess of permanganate crystals, a little at a time. The reaction is very rapid in moderately dilute solutions, and unless capacious platinum basins are available it is necessary to transfer to a flask, and to dilute and boil with more permanganate if necessary, to completely decompose the alloy. The determination is then finished as usual.



As an alternative one may proceed as in Method IV. for the estimation of tungsten so far as evaporation to sulphuric fumes ; then dilute, boil with permanganate, and finish as before. The tungstic oxide may be previously filtered off for the determination of tungsten, if required, but the small amount of chromium it invariably contains, if not boiled with hydrochloric acid, must be separately estimated.

## NICKEL-TUNGSTEN.

### Carbon.

Direct ignition in a stream of oxygen may leave what appears to be a completely oxidized residue ; but simple ignition is unreliable, even when the alloy contains as much as 75 per cent. tungsten. The powdered alloy should be ignited with red lead. Comparative experiments with lead chromate showed that this reagent could not be invariably relied upon to complete the oxidation.

### Silicon, Manganese, Sulphur, and Phosphorus.

These elements are determined as in ferro-tungsten alloys.

### Tungsten.

As in ferro-tungsten alloys. The most convenient methods are III. and IV. From the nitro-fluoric solution the nickel very readily deposits well-formed green crystals.

### Nickel.

The iron is separated or not as occasion demands in the filtrate from the tungstic oxide (preceding estimation), and the nickel estimated cyanometrically. If the alloy contains only small amounts of iron a very rapid determination of the nickel can be made by dissolving in nitro-fluoric acid, pouring at once into an excess of ammonia, and titrating a portion of the filtrate with potassium cyanide. For details see estimation of nickel in steel and in alloys.

## METALLIC TUNGSTEN POWDERS.

### RAPID EVALUATION.

The determination of, or the search even for every minor constituent of a tungsten powder has perhaps never been made ; partly because no works' management requires such an analysis, but mainly, we



imagine, on account of the difficulty of making it. The tungsten assay of the high-grade powders used for steel making can be rapidly made in the following manner. The results are tolerably accurate, varying rarely more than a half per cent. from the actual truth: the tendency is for them to be too high.

Weigh three grams of the powder into a tared platinum dish<sup>1</sup> and heat in the muffle. Soon after ignition begins withdraw the basin in order to observe the more or less distinct smell of sulphur dioxide according to the amount of sulphur there is present. The colour of the oxidized sample should also be observed: a distinctly green tinge indicates the presence of sodium tungstate, although this component may be present in small amounts without causing a green colour. When completely oxidized allow to cool, moisten with hydrofluoric acid, evaporate, ignite strongly, and weigh. Half fill the basin with water, add a piece of caustic soda half the size of a walnut and heat to boiling: this loosens the residue from the basin. Transfer to a beaker, boil until only a brown precipitate remains undissolved, then dilute to about 300 c.c., and allow the precipitate to subside. Filter through pulp, dissolve the iron stain from the platinum dish with hydrochloric acid, precipitate its solution with ammonia, and collect on the same filter. Wash, ignite, and weigh. Dissolve the precipitate in 5 to 10 c.c. hydrochloric acid, boil until tungstic oxide begins to separate, dilute to four or five times its bulk with water, collect the precipitated tungstic oxide and deduct the amount of it from the previously weighed precipitate. The difference subtracted from the weighing first made gives the weight of oxide equivalent to the total tungsten in the powder. An example will make the operations clearer:

Weight of dish, -	-	-	-	-	-	22.9400.....(1)
Ditto + 3 grams powder after HF. treatment, -	-	-	-	-	-	26.4823.....(2)
Residue insoluble in caustic soda, -	-	-	-	-	-	0.0703.....(3)
Oxide from hydrochloric acid solution, -	-	-	-	-	-	0.0400.....(4)
(3) - (4), -	-	-	-	-	-	0.0303.....(5)
(2) - (1) =	3.5423					
(5) =	0.0303					
<hr/>						
$3.5120 \times \frac{.7931}{3} = 92.8 \text{ per cent. tungsten.}$						

<sup>1</sup> If the powder is heaped in the centre of the dish it oxidizes slowly, and also, if the muffle is very hot, forms an alloy with the platinum which complicates subsequent operations. The powder should be spread over the dish in as thin a layer as possible and heated, to begin with, at low redness.

An approximate result, involving less trouble but more likely to be falsified by any alumina present, is obtained by fusing the residue with two or three times its bulk of sodium carbonate, instead of boiling with caustic soda. The melt is dissolved in water and the insoluble oxides collected, washed, and weighed. This weight is deducted from that of the mass before fusion and the difference calculated to percentage of total tungsten.

## COMPLETE ANALYSIS.

### Carbon.

Ignition in a stream of oxygen yields all the carbon as dioxide. It may vary from traces up to five per cent. In the latter case it consists mostly of the excess of charcoal used in reducing the metal.

### Manganese.

As in ferro-tungsten alloys. This element is sometimes altogether absent.

### Phosphorus.

As in ferro-tungsten alloys. If the fusion process is used a little ferric solution should be added after filtering off tungstic oxide in order to form basic ferric phosphate on adding ammonia.

### Sulphur.

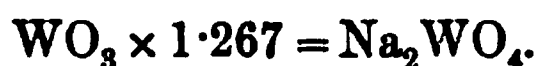
As in ferro-tungsten alloys. Most of the sulphur passes into solution when two and a half grams are treated like a steel (page 43) although the material is by no means completely decomposed. The former and latter processes have generally given concordant results, but now and again the aqua-regia treatment leaves considerable sulphur in the residue. A similar objection is probably the only one to be raised against the powder being boiled with hydrochloric acid and the evolved sulphuretted hydrogen absorbed and determined.

### Water.

Water is always present if the powder contains lime. It cannot be driven off in the water bath, but must be carried forward into a weighed calcium chloride tube after heating the sample to redness in a stream of dried air (see page 202). The determination can be made with reasonable accuracy by heating three grams of the powder in a closed tube so as to drive the water beyond a certain constriction. The tube is then nicked, broken off at the narrowed part, weighed, dried, and re-weighed (Richards).

**Sodium Tungstate.**

Boil three grams of the powder with 100 c.c. water and a few crystals of ammonium nitrate. Filter through a little pulp and re-boil the residue in the same way. Acidify the combined filtrates with acetic acid, and add a solution of lead acetate. Collect the precipitated lead tungstate, wash, and ignite at so high a temperature only that the paper is readily destroyed. Transfer the residue to a small beaker, dissolve in a small quantity of hydrochloric acid, evaporate to low bulk but not to dryness, dilute with water, collect the resulting tungstic oxide, ignite and weigh



Ammonium nitrate is added during the extraction merely to prevent tungstic oxides passing the filter. Five separate estimations made in this way on different weights of the same powder gave: on one gram, 1.27; on two grams, 1.27 and 1.30; on three grams, 1.27; and on five grams, 1.14 per cent. sodium tungstate.

**Tungstic Oxide.**

The blue-coloured solution sometimes obtained when powders are boiled with water shows that lower oxides of tungsten are present. The estimation of these oxides in a separate form is impracticable if not altogether impossible. The following process takes account of tungstic oxide only; any other oxides it may affect are calculated as tungstic oxide.

Pour 30 c.c. hot concentrated hydrochloric acid over three grams of powder and digest a few minutes with constant agitation so as to break down any compounds of tungstic and ferric oxides not attacked by caustic soda. Pour the acid solution through a small filter, wash once with water, and set the filtrate evaporating in a small basin. To the residue add 50 c.c. binormal caustic soda, and boil for five or ten minutes. Pour through the previously used filter and wash the residue with hot water containing a few crystals of ammonium nitrate. Add a drop of methylorange to the filtrate and a faint excess of nitric acid, then a drop or two of ammonia, 2 c.c. acetic acid and an excess of lead acetate.

When the precipitated lead tungstate has settled, decant off the clear solution and pour the residue into the evaporating hydrochloric acid. When the acid solution is nearly dry add dilute hydrochloric acid (1 to 5), collect the oxide and weigh. The equivalent of the previously determined sodium tungstate is deducted, and the remainder expressed as per cent. tungsten trioxide.

It is widely believed that metallic tungsten is considerably attacked by even dilute caustic soda. In order to establish the value of this impression a powder, after the foregoing treatment, was boiled four times successively with binormal caustic soda. The following amounts of tungstic oxide were obtained :

	Grams $WO_3$	Per cent. $WO_3$
1.	0·0060	0·20
2.	0·0043	0·14
3.	0·0034	0·11
4.	0·0028	0·09

These additional amounts of tungstic oxide may be due to the action of caustic soda on the metal or to its action on oxides not previously removed, or more probably to both causes. We propose to take the result obtained by one boiling with caustic soda, and to admit that it is uncertain to two or three tenths per cent.

If the labour involved were not more than the additional accuracy was worth it would be more satisfactory to make (say) four successive boilings, and deduct three times the amount of oxide recovered from the last boiling from the sum of the other three on the assumption that it represents the action of caustic soda on the metal only. Extended determinations of this kind give results which agree well within 0·20 per cent. with those obtained by one boiling.

Three grams of a powder boiled with strong hydrochloric acid after repeated caustic-soda treatments gave only 0·0032 grams tungstic oxide.

#### **Tungsten and Molybdenum.**

The total tungsten may be estimated by Methods I., II., or best of all, IV., of those given for the estimation of tungsten in alloys. It needs a large quantity of acid and considerable skill to get one gram of metallic tungsten into solution by method III., and we do not recommend it except when molybdenum is to be estimated also. Method IV., it may be remarked, cannot be used for the estimation of molybdenum as well as tungsten as the fluoride of the former metal is volatile.<sup>1</sup> Method I. may, however, be used, the molybdenum being estimated as already described after filtering off tungstic oxide.

By a more refined modification of the process used for the rapid

<sup>1</sup> It is just possible that if sulphuric acid were added before the hydrofluoric molybdenum might not be volatilized.

evaluation of these powders the tungsten may be very accurately estimated, and some of the minor constituents also, viz. :

#### **Silica, Iron, Alumina, and Lime.**

Ignite three grams of the powder in a platinum dish as before (page 151), and continue the ignition in a hot muffle until a constant weight is reached ; *i.e.* until oxidation and decarbonization are complete. After weighing treat with hydrofluoric acid and re-weigh : the loss represents silica.<sup>1</sup> Fuse the residue with sodium carbonate, extract with water, and allow the diluted solution to stand in a warm place in a porcelain or, better still, platinum or nickel vessel for several hours, preferably over night. This pause is desirable in order to allow small amounts of iron which are invariably dissolved by the soda to separate out : then filter.

A current of carbon dioxide is passed into the filtrate to perfect saturation : any small precipitate of alumina and lime is collected, gently ignited, weighed, and added to the insoluble ferric oxide, etc.

In calculating the percentage tungsten the combined weights of the alumina, lime, and ferric oxide are deducted from the residue weighed after eliminating silica. From the calculated tungsten percentage there must also be deducted 0.21 per cent. for each 1.0 per cent. sodium tungstate the powder contains. A still further correction is needed if considerable amounts of bronze crystals are present : see Estimation of Tungsten Bronze.

The precipitate consisting of lime, alumina, and ferric oxide is dissolved in hydrochloric acid (assisted by fusion if necessary) and the separate bodies estimated as in refractory materials.

The necessary variation in the above scheme in case manganese is present needs no special mention.

#### **Tungsten Bronze.**

After boiling a powder with caustic soda small red or yellow crystals may always be seen. We have never examined a powder from which these crystals were entirely absent : in one powder at least we have observed approximately ten per cent. They may be isolated by passing a suitably selected powder through a sieve of sixty meshes to the lineal inch. The impure crystals retained by the sieve are then boiled with caustic soda and washed so as to remove adherent powder. After drying digest with nitro-fluoric acid, which speedily dissolves the

<sup>1</sup> Theoretical objection may be taken to determining silica in this way, but the results are practically accurate.

metallic tungsten and a portion also of the crystals: the residue is washed and boiled again with soda.

These crystals exist as cubes and tetrahedra, and when purified in the above fashion have a specific gravity of about 7.3. Their mode of formation is made evident by recalling the fact that the tungstic oxide used in the manufacture of metallic powders is rarely free from sodium tungstate.

No method is known of isolating these crystals quantitatively. Unsuccessful attempts have been made by igniting the residue from the sodium tungstate estimation, and then again digesting the oxides with dilute ammonium nitrate, on the assumption that the soda of the bronze would have formed sodium tungstate. The following procedure enables their amount to be approximately gauged.

Dissolve two and a half grams of powder in a capacious platinum dish with nitrofluoric and sulphuric acids. Allow the evaporation to proceed slowly, so that the tungsten bronze may be completely decomposed, but heat finally until the solution fumes strongly, then boil and filter. Add a small excess of ammonia and a little ammonium oxalate to the filtrate, and remove the precipitated lime, alumina, and ferric oxide. Evaporate the clear solution to dryness, and weigh the residue as  $\text{Na}_2\text{SO}_4$  after driving off volatile ammonium salts. From the amount of alkali thus determined deduct the equivalent of the sodium tungstate and calculate the remainder to tungsten bronze.

The factor for converting the sodium found to tungsten bronze depends upon which of the numerous bronzes it is that happens to be in the powder. At least four soda-tungsten bronzes are known besides potash and lithia bronzes: they are

Colour.	Composition.	Per cent. Sodium.
Purple-Red, - - -	$\text{Na}_2 \cdot 3\text{WO}_3$	6.20
Red-Yellow, - - -	$2\text{Na}_2 \cdot 5\text{WO}_3$	7.35
Golden Yellow, - - -	$5\text{Na}_2 \cdot 12\text{WO}_3$	7.63
Blue, - - - -	$\text{Na}_2 \cdot 5\text{WO}_3$	3.81

From the above considerations a satisfactory means of estimating the amount of tungsten bronze appears to await a mechanical separation not yet discovered.

#### Tin.

This is a minor impurity of tungsten powders. The following mode of estimating it is given: Heat the powder to complete oxidation in a porcelain crucible, and mix with four times its weight of previously

fused and powdered potassium cyanide. Keep the mixture in quiet fusion for a time, then cool, extract with water, and weigh the collected beads of metallic tin. This process has not given us satisfactory results ; we have the matter under investigation at present.

### Niobium.

This element has been occasionally referred to as a constituent of tungsten powders, but no one has thought it worth saying in what amounts it may be expected to occur, or how it may be estimated. Bernoulli (*Chemical News*, v. 116) separates it from tungsten by fusing with sodium carbonate, filtering off insoluble metallic oxides, precipitating the filtrate with lead acetate, digesting the moist lead tungstate with ammonium sulphide, removing the sulphide of lead, and evaporating the filtrate with nitric acid nearly to dryness. On adding an excess of ammonia, tungstic oxide goes into solution and leaves niobic oxide behind. We have had no experience of this separation.

### Specific Gravity.

Comparisons of specific gravity are frequently made by users of tungsten who know, and sometimes care, very little about chemical analysis. A narrow graduated tube is obtained and filled to a convenient mark with water ; a fairly large quantity of powder is then added, and the whole shaken. The level of water is then read off, and either the specific gravity calculated or, more often, the bulk occupied compared with that observed in relation to some particularly satisfactory powder the user has in mind. Tons of powder used to be regularly bought according to the results of this crude test.

To determine the actual specific gravity first note the weight of a 25 c.c. specific gravity bottle when filled with water at 15° C., or as near that temperature as is practicable.<sup>1</sup>

Weigh five grams of powder into the empty bottle, cover it with water and boil a minute or two, then cool to the former temperature, fill the

<sup>1</sup> The correction for difference of temperature can easily be made from a table of water expansions. The following extract from Kopp's tables meets the requirements of this case :

Temperature.	Volume.
0°C	1·0000
5	·9999
10	1·0001
15	1·0007
20	1·0016
25	1·0027
30	1·0041

for an ordinary steel, but diluted with about its own volume of water, so that molybdic acid shall be less readily precipitated. With the lower percentage alloys the solution is at most only faintly opalescent after the permanganate oxidation, and in such cases no serious error can creep in by finishing the estimation as usual. With richer alloys, fused molybdenum metal for example, the solution may at the same stage or even earlier be turbid, partly on account of the formation of the usual phospho-molybdate, and partly on account of separated molybdic oxide.<sup>1</sup> When this happens, and whenever else there is reason to fear molybdic oxide contamination, the precipitate is filtered off, washed, dissolved in ammonia and the phospho-molybdate re-precipitated after acidifying with nitric acid.

### Iron.

On precipitating with ammonium hydrate, part of the molybdenum accompanies the iron; gravimetric estimations are therefore too high. The iron cannot be estimated by simply dissolving the alloy and titrating, because the molybdenum, reduced to sesqui-oxide by the nascent hydrogen, falsifies the result by being re-oxidized to trioxide during the titration. For this reason, too, ferric solutions containing molybdenum should not be reduced with stannous chloride or zinc. They may, however, be reduced with sulphur dioxide and titrated accurately either with bichromate or permanganate. Ferro-cyanide will not satisfactorily indicate iron on account of the very ready formation of a deep brown precipitate with solutions of molybdic oxide.

### NICKEL-MOLYBDENUM.

These alloys generally contain very little iron, so that after decomposing the sample with aqua regia, the solution is poured into an excess of ammonium hydrate. If more than a few tenths per cent. of iron are present, the precipitate contains small amounts of nickel and molybdenum, which may be eliminated by a second precipitation. The molybdenum may then be precipitated from a portion of the combined

<sup>1</sup> The tendency of molybdic oxide to precipitate is not very pronounced when only small amounts of phosphorus are present, provided that the sample be dissolved in the diluted acid. Thus, in a sample of fused metal containing 92.4 per cent. molybdenum, but only 0.006 per cent. phosphorus, there was obtained only 0.028 per cent. phosphorus, when the molybdic acid which was precipitated by boiling and oxidation was collected along with the yellow precipitate of ammonium phospho-molybdate.



filtrates without separating the nickel (p. 85), and the nickel may be cyanometrically estimated without separating the molybdenum (140). When considerable quantities of iron are present, the molybdenum should be separated as in the analysis of steels for this element, *i.e.* by means of caustic soda, and the nickel and iron separated afterwards in a fresh sample for the estimation of the nickel. The latter separation may be effected with the greatest facility by means of ammonia, a process which depends for its success upon the fact that the iron is precipitated as basic ferric molybdate when considerably less ammonia is added than would make the solution alkaline (see p. 76 *et seq.*).

### METALLIC MOLYBDENUM POWDERS.

We have never met with a sample of molybdenum powder containing, according to the vendor's valuation, less than 95 per cent. of molybdenum; we have found very few which contained as much as 90 per cent.

An estimation of each of the elements or combination of elements in a commercial powder would be a very difficult piece of work, as, besides metallic molybdenum, there may be present such bodies as molybdenum trioxide, mixtures of the lower oxides of molybdenum, metallic tungsten, oxides of tungsten, silicon, aluminium, iron, ferric oxide, combined carbon, graphite, charcoal, sulphur, and water. It is certainly desirable, if powder continues to be the form in which the metal is supplied to steel manufacturers, to have more or less ready means of submitting the material to a complete examination. We are disposed, however, to make ourselves responsible only for such processes as may be used to determine the more important constituents.

#### Carbon.

The total carbon is readily determined by direct combustion in oxygen, or with less fear of choking the tube if along with some reagent to fix the volatile oxide. Moissan determines the combined carbon by attacking the sample with acids, passing the gases over copper oxide, etc., into caustic potash, the graphite being estimated in the insoluble residue. In these powders it is impossible to distinguish by any simple means the graphite from the excess of charcoal which has been used in the reduction. In the fused metal the ordinary method for estimating graphite in pig iron can be used.

### Molybdenum.

For the estimation of the chief element the powder may be mixed with sodium carbonate, and a small quantity of nitre to promote oxidation, placed in a platinum crucible under a layer of sodium carbonate, and heated over the blowpipe until decomposed. The bottom only of the crucible should be red hot, so as to avoid loss by volatilization. After extracting with water, the molybdenum and any associated tungsten are precipitated in the filtrate from the insoluble ferric oxide, etc., with lead acetate, and separated as described on p. 85. A more complete examination is favoured by opening out with aqua regia, fusion of the residue with nitre, and evaporation of the mixed solutions so as to separate silica and tungstic oxide. A portion of the main filtrate is used for the estimation of molybdenum after separating the small amounts of iron and aluminium with ammonia, another portion for the estimation of sulphur, etc.

### Oxygen.

The better varieties of powder are grey and anhydrous; the poorer qualities are black and may contain five or six per cent. of water. Owing to imperfect reduction in the first instance or to subsequent oxidation through exposure, molybdenum powders may contain, besides the metal itself, the oxides  $\text{Mo}_2\text{O}_3$ ,  $\text{MoO}_2$ ,  $\text{MoO}_3$ , and  $\text{Mo}_3\text{O}_8$ . The blue oxide ( $\text{Mo}_3\text{O}_8$ ) or its hydroxide is soluble in water, so that merely shaking the sample with water serves for its identification; it is frequently present in the inferior black powders. The chief oxide is  $\text{MoO}_3$ . We are not acquainted with any method of precisely separating this oxide from the others, but an approximation to its amount may be obtained by boiling one gram of the powder with 100 c.c. of binormal caustic soda solution for five or ten minutes, filtering, and precipitating the molybdenum from the filtrate. The oxygen is then calculated on the supposition that the molybdenum dissolved out existed as the trioxide. Metallic molybdenum is practically insoluble in caustic soda, and according to *Comey's Dictionary*, so also are  $\text{Mo}_2\text{O}_3$  and  $\text{MoO}_2$ ; hence the figure obtained would always err on the negative side. The treatment with caustic alkali occasionally results in the formation of a precipitate of lead sulphide when lead acetate is added for the estimation of the molybdenum. In such an event the acidified filtrate must of course be well boiled to expel sulphuretted hydrogen before precipitating.<sup>1</sup> The following are typical analyses of commercial molybdenum

<sup>1</sup> Both molybdenum and its oxide  $\text{MoO}_2$  quantitatively reduce ammoniacal silver solutions. As silver can be estimated so easily and accurately, the indirect deter-

alloys : I. and II. are powders, III. and IV. alloys with nickel, V. a ferro-molybdenum, and VI. the fused metal.

	I.	II.	III.	IV.	V.	VI.
Molybdenum, - -	72.62	86.72	70.53	36.75	16.69	92.40
Tungsten, - -	3.17	nil	1.27	—	1.53	0.74
Nickel, - - -	—	—	21.60	57.80	—	—
Iron, - - -	1.60	0.48	3.08	1.60	76.34	2.73
Carbon, - - -	7.80	8.18	2.94	1.08	4.20	3.87
Silicon, - - -	—	—	0.42	0.14	0.39	0.05
Silica, - - -	—	1.57	—	—	—	—
Manganese, - -	—	nil	0.40	trace	0.37	nil
Sulphur, - - -	—	0.10	trace	3.00	0.076	0.33
Oxygen, - - -	8.30	1.00	—	—	—	—
Water, - - -	4.30	—	—	—	—	—
	97.79	98.05	100.24	100.37	99.596	100.12

VANADIUM ALLOYS.

FERRO-VANADIUM.

Commercial ferro-vanadiums often contain comparatively large amounts of sulphur, phosphorus, aluminium, and copper, which either occur naturally in the raw material or have been purposely added to facilitate manufacture. As with alloys of molybdenum so also in the case of ferro-vanadiums, their acceptance at the valuation of the vendor is to some extent responsible for the variety of conclusions respecting the properties which vanadium confers upon steel. We have met with steels made from the best Swedish materials containing less than 0.5 per cent. of vanadium with nearly as much as 0.1 per cent. of phosphorus. The typical analyses I. and II. appended are of alloys which at the time (1901) were supposed to be very good ones.

Carbon.

This element may be determined in ferro-vanadium by direct ignition in a current of oxygen when the alloys contain as little *mination* of the oxygen of a powder would appear a simple affair. Unfortunately, *however*, with such highly carburetted (and sometimes sulphuretted) material as *these* powders, the results are always too high. It is possible to distinguish by *this* test a poor from a rich sample, but otherwise the test is exceedingly *crude*. See Friedheim and Hoffmann, *Jour. Soc. Chem. Indust.* 1902, 426.

as 10 per cent. of vanadium. The alloys may, however, be easily decomposed by a solution of cuprammonium chloride, a portion only of the vanadium remaining with the carbonaceous residue.

#### Silicon and Sulphur.

The sulphur may be determined by the aqua-regia-barium-sulphate process as for steels. The solution from which the precipitation as barium sulphate is made should be decidedly acid so as to avoid the precipitation of insoluble vanadates of barium and iron. The silicon is determined with sufficient exactitude by extraction of the ignited residue with hydrofluoric acid.

#### Manganese.

The bismuthate process as carried out for steels gives good results, but particular care must be taken to destroy the carbonaceous matter completely in the hot initial solution, so that only the slow oxidation of the blue hypovanadate and not the presence of carbon is accountable for the permanganate used during the titration.

The gravimetric estimation of the manganese as trimanganic tetroxide after separation of the iron with an acetate is somewhat troublesome. There is considerable uncertainty in the 'neutralization' owing to the formation of a basic ferric vanadate of a light brown colour; which may or may not, according to the amount of vanadium present, contain the whole of the iron. When this precipitate begins to form or (if large amounts of vanadium are present) when an appreciable precipitate has formed, heat the solution to boiling point and add as little acetate as suffices to effect the complete precipitation of the iron. To do this effectively, remove the flask from the burner, allow the precipitate to settle, and if the supernatant liquid is not colourless add a few c.c. more strong ammonium acetate and re-boil. Repeat this operation until the precipitation is apparently complete. In this way the whole or nearly the whole of the vanadium is carried down with the precipitated iron<sup>1</sup> instead of passing into the filtrate to subsequently contaminate the hydrated oxide of manganese.

#### Phosphorus.

The large amounts of phosphorus which the analyst finds in these alloys and the undesirable amounts of that element found in vanadium steels that have been made from pure irons have led many people to

<sup>1</sup> Conversely, the separation of iron and vanadium by repeated acetate precipitations depends on the addition of *large* amounts of acetate, so as to bring about the formation of basic *acetates* of iron in preference to basic *vanadates*. Under the best conditions the separation is a very unsatisfactory one.

conclude that vanadio-molybdates are precipitated along with the yellow phospho-molybdate, and the results are therefore enormously exaggerated and in consequence altogether unreliable. The only piece of experimental evidence in favour of this conclusion is the fact that when formed in hot solutions in the ordinary way the phospho-molybdate has an orange-red colour and certainly does contain vanadium, whilst when precipitated from cold solutions it has a similar colour and is soluble in dilute nitric acid.

In a large number of experiments made with steels containing from 0.01 to 0.10 per cent. of phosphorus, and from 0.30 to 5.5 per cent. of vanadium introduced as ammonium metavanadate, we found, proceeding as usual for the estimation of phosphorus, that the ammonium phospho-molybdate always had an orange-red colour more or less intense according to the greater or less amount of vanadium present, adhered more or less tenaciously to the sides of the vessel, and always actually contained vanadium. Nevertheless the results obtained were less than those obtained from the same steels in the absence of vanadium. The ammoniacal solution of the ammonium phospho-molybdate was re-precipitated by pouring into an acetic acid solution of lead acetate, so that the vanadium might be precipitated as a basic vanadate, probably  $2\text{Pb}_2\text{V}_2\text{O}_7 \cdot \text{PbO}$ , along with the molybdenum and phosphorus as  $24\text{PbMoO}_4 + \text{Pb}_3(\text{PO}_4)_2$  (see p. 58). The results were from 0.002 to 0.005 per cent. low. The presence of vanadium in the lead salts may be easily detected; on adding cold concentrated hydrochloric acid a reddish-brown colour at once appears, and this changes to green on heating. This green colour is, however, by no means distinct when very small amounts of vanadium are present.

It may be concluded then that the presence of vanadium retards the formation of phospho-molybdates, and thus leads to low results when the estimation of phosphorus is conducted as usual. The deficiency is not very serious, as it is partially compensated for by the vanadium, which is ultimately weighed as basic pyrovanadate of lead and included in the calculation as lead molybdate. But the orange-red colour, which shows when very small amounts of vanadium are present, and which may perhaps constitute a serviceable indication of the presence of that element in material in which its existence is not suspected, is an offence to the eye, and is continually suggesting that something is wrong. We therefore suggest the following procedure:

Dissolve two grams of the steel or alloy in 45 c.c. nitric acid (1.20), add an excess of permanganate and clear with ferrous sulphate, as in the estimation of phosphorus in ordinary steels. Then cool and add

a small excess of a strong solution of ferrous sulphate, so that a drop of the solution tested with ferri-cyanide gives an *immediate and marked* blue colour. Then add 6 or 7 c.c. strong ammonia and the usual amount of the molybdate reagent, and shake occasionally in a stoppered flask for half an hour or so. By this time nearly all the phosphorus will have been precipitated in the usual form of the yellow precipitate uncontaminated with vanadium. The ferrous sulphate serves to reduce the vanadate to hypovanadate ( $V_2O_5$  to  $V_2O_4$ ), in which form it does not interfere with the precipitation of the phospho-molybdate. In order to destroy the excess of ferrous sulphate and to complete the precipitation of the phosphorus, it may be advisable to heat the solution to  $60^\circ$  for half an hour or so, but, and particularly when the amount of phosphorus is considerable, the precipitation is practically complete in the cold. The yellow precipitate is then filtered off and estimated as usual.

With a number of alloys containing large amounts of phosphorus, two portions of the cold solution just cleared with ferrous sulphate were measured off, and the phosphorus in one precipitated from the hot, and in the other from the cold solution after reducing the vanadium as described above. The cold precipitation always gave the higher results and the precipitates were free from vanadium. Two examples are appended :

	I. 10 per cent. Vanadium.	II. 16 per cent. Vanadium.
Hot Precipitation, -	0.61 per cent. P.	1.28
Cold           ,,       -	0.65   ,,       ,,	1.35

To dissolve the orange-red precipitates obtained from hot solutions and re-precipitate to eliminate vanadium leads away from, rather than towards the truth. It would appear that highly complex compounds are formed containing the phosphorus, molybdenum and vanadium, which are more soluble than the ordinary ammonium phospho-molybdate, and that, within wide limits, the vanadium precipitated corresponds approximately to the phosphorus held in solution.

#### Aluminium and Copper.

Pour 60 c.c. hot sulphuric acid (1 in 6) over two grams of the alloy and keep boiling, leaving an exit only for the steam until the sample is decomposed. Filter and wash. The filtrate may contain a little of the copper, and is certain to contain some vanadium as well as

practically all the iron and aluminium. Pass sulphuretted hydrogen through the diluted solution, collect any precipitated copper sulphide and reserve it. Boil off the sulphuretted hydrogen from the filtrate, and if not too much vanadium has passed into it, add sodium phosphate and then ammonia until a precipitate just forms. Clear with hydrochloric acid, dilute to about 300 c.c., add ten grams of sodium thiosulphate, and 20 c.c. of acetic acid, and then boil, filter, and wash as in the estimation of aluminium in steel. The ignited phosphate of aluminium, besides a small quantity of iron, may also contain some vanadium. By dissolving in hydrochloric acid and re-precipitating with phosphate and thiosulphate, the iron is removed, but vanadium may still be present, although, if the precipitate is snow-white the amount of vanadium will be exceedingly small. Its presence is at once indicated by the red colour which forms on the addition of concentrated hydrochloric acid. If the amount of vanadium associated with the final precipitate is judged to be prejudicial to the accuracy of the aluminium estimation, as it certainly is if alloys of low carbon contents are being assayed, then a special separation of the vanadium and aluminium must be made as follows:

To the hydrochloric acid solution of the ignited phosphate add one gram of sodium phosphate, and sodium peroxide until the reddish brown colour due to the presence of vanadium is fully developed, then add a small excess of ammonia and boil. Allow the aluminium phosphate to settle; filter, wash, and set the paper and precipitate to digest in dilute hydrochloric acid. To the filtrate add an excess of acid, boil until the colour disappears, and then add a slight excess of ammonia and boil again. If the solution remains clear it may be rejected, but if a precipitate forms, collect it on a pulp filter, then pour over it the hot dilute hydrochloric acid solution of the main precipitate and wash. In order to eliminate traces of iron which were not completely washed from the first thiosulphate precipitate or which may have been introduced with the sodium peroxide, the solution is re-precipitated with phosphate and thiosulphate, and the resulting aluminium phosphate ignited and weighed. It should now be quite white, and contain not more than a trace of vanadium.

The residue which was unattacked by the boiling dilute sulphuric acid contains practically all the copper and some vanadium. Ignite it well and then dissolve it in hydrochloric acid. Filter off the silica which is left undissolved, pass a current of sulphuretted hydrogen, collect the copper sulphide on the filter previously used for the same purpose, and proceed with the estimation of the copper in the manner already



described for steels on p. 102. It is essential to exactitude that the copper solution which is treated with potassium iodide and then titrated with thiosulphate should contain no vanadium, as vanadates are reduced by the iodide.

### Vanadium.

1. **Estimation in the Presence of the Iron.**—The momentary appearance of the pink colour which is observable in the case of steels when all free ferrous iron has been oxidized by permanganate whilst the vanadium has as yet been unattacked, cannot be so clearly distinguished in solutions of alloys, as the larger amounts of hypovanadic acid are more readily attacked by the oxidant. On the other hand, the estimation of vanadium by adding ferrous sulphate until a spot test with ferri-cyanide gives a blue colour, or by adding an excess of ferrous sulphate and going back with bichromate or permanganate, or by measuring the amount of permanganate necessary to the formation of a permanent pink tinge from the point at which ferri-cyanide gives no blue colour, is sufficiently accurate in any of these modifications of Lindemann's process.

Dissolve 0.25 to 1 gram of the powdered alloy in 20 c.c. (1 in 6) sulphuric acid, with the addition of a little nitric acid to complete the decomposition and oxidize the iron, and also a little permanganate so as to destroy all the carbonaceous matter. After boiling, clear with hydrogen peroxide, boil to destroy the excess, and cool. To the cold solution add one or two drops of permanganate, so as to make certain that all the vanadium is in the condition of vanadic acid; if the pink colour disappears add more permanganate until it persists. Now run in decinormal ferrous ammonium sulphate from a burette until the spot test with ferri-cyanide gives an immediate blue colour, and note the reading of the burette. Add a few c.c.'s ferrous solution in excess, and titrate back again with permanganate until the spot test with ferri-cyanide ceases to be blue; read the burettes again. Now run in permanganate until a permanent pink colour is formed, and once again take the readings. These three readings should fully determine the percentage of vanadium in the alloy.

$$1 \text{ c.c. } \frac{N}{10} \text{ solution} = .00512 \text{ gram vanadium.}$$

When working on half a gram of an alloy containing say 15 per cent. of vanadium, one may readily observe the interference of blue hypovanadic solutions with the ferri-cyanide spot indicator, which makes the process quite useless for estimating vanadium in steels. To minimize



this interference as much as possible the titrated liquid may be tested with ferri-cyanide by taking small drops only in the first place. Later, much larger drops must be taken and will be found to show no colour when the smaller drops have become distinctly blue. The converse of this would happen if pure ferrous solutions were being titrated. For a similar reason the ferrous sulphate should be added until a blue colour forms *immediately* on making the test.

2. **Estimation after Separation of the Iron.** (a) *In the wet way.*—The separation by boiling with dilute sulphuric acid can be made satisfactorily only with such alloys as contain considerable amounts of carbon, *i.e.* two or three per cent. Many ferro-vanadiums contain very little carbon, and consequently most of the vanadium goes into solution. It is best then to proceed as in the process described on p. 92 for estimating vanadium in irons or as follows:

(b) *In the dry way.*—Mix from 0.25 to 1 gram of the powdered alloy with several times its weight of sodium carbonate and a little potassium nitrate, and fuse the mixture in the muffle in a shallow dish. At first the dish should be covered to prevent loss, but later the cover may be removed and the fusion continued till action ceases. Then cool, digest with water, filter off the ferric oxide, and titrate the filtrate with ferrous sulphate and permanganate as previously described. By leaving nitre out of the fusion mixture and adding a little permanganate, if the alloy is poor in manganese, to promote oxidation, the filtrate of the aqueous extract may be acidified with sulphuric acid, reduced with sulphurous acid, and titrated with permanganate.

The ferric oxide filtered off sometimes contains a little of the vanadium, either on account of imperfect decomposition in the fusion or on account of imperfect washing. Ignite it therefore to destroy the paper, dissolve in as small a quantity as possible of concentrated hydrochloric acid, add sulphuric acid, and evaporate to thick fumes. Then cool and add hydrogen peroxide, making the test quantitative if necessary, in the manner already described in connection with the estimation of vanadium in steel.

### Iron.

After applying the peroxide test, the solution may be made up to a definite volume and an aliquot part reduced with sulphur dioxide and titrated with permanganate. A sulphuric and not a nitric acid solution of the peroxide should of course be used for the previous test.

## TYPICAL ANALYSES.

	I.	II.	III.	IV.
Carbon, - - -	1·86	0·02	0·04	0·10
Silicon, - - -	0·85	1·74	0·84	1·84
Manganese, - - -	1·90	3·08	0·28	traces
Sulphur, - - -	0·14	0·19	0·21	0·09
Phosphorus, - - -	0·65	1·35	0·34	2·10
Vanadium, - - -	10·84	16·10	33·00	42·85
Aluminium, - - -	1·77	1·30	0·20	nil
Copper, - - -	2·10	2·64	nil	nil
Iron, - - -	79·90	73·52	65·10	53·17
	100·01	99·94	100·01	100·15

## TITANIUM ALLOYS.

## FERRO-TITANIUM.

Ferro-titanium is frequently made by fusing a mixture of scrap iron, titaniferous ore and aluminium in an electric furnace. The alloy is not much used for steel-making, and there are no well-worn methods for the analysis of it. In the few alloys we have handled the main constituents have been determined in the following manner; but a short experience shows that there are several ways in which the analysis may be conducted, and that a complete analysis is not so difficult as is often supposed.

**Carbon.**

This element may be determined by ignition with red lead; the surface of the fused residue has a dull chocolate colour. Equally good results have been obtained by igniting the powder alone in a stream of air or oxygen, but we have not examined a sufficiently great variety of samples to enable us to assert safely that mere ignition in the absence of a solid oxidizing agent will always completely decarbonize the alloy.

**Manganese.**

The alloy is decomposed with nitric acid (1·20), with the addition, if necessary, of a few drops of hydrofluoric acid. The organic matter is destroyed in the hot solution with sodium bismuthate and the estima-

tion completed, after cooling, by oxidation with bismuthate and titration of the filtrate with ferrous sulphate in the usual manner. The excess of bismuthate has a slight tendency to pass the filter, and the end of the titration is not quite so stable as usual. The oxidation of the nitro-sulphuric solution with red lead (p. 32) works very smoothly, and the end reaction with ferrous sulphate is quite sharp.

### **Sulphur.**

Ferro-titaniums generally dissolve completely in dilute hydrochloric or sulphuric acid to a lilac-coloured solution. If no sulphuretted hydrogen can be smelt and lead acetate paper is not more than slightly discoloured, it is unnecessary to proceed further. An actual estimation may be made by the evolution process as used for steels or by the following gravimetric procedure. To one gram of the powdered alloy add two or three grams of pure potassium chlorate crystals and some warm water, and then gradually add hydrochloric acid until the decomposition is complete. After boiling off chlorine, dilute slightly, add a small excess of ammonium hydrate, filter, and wash. To the acidified filtrate add barium chloride, and eventually collect and weigh the barium sulphate. The original precipitate contains the iron, titanium, aluminium, and phosphorus, and may be subsequently used for the estimation of one or more of these elements.

### **Titanium, Silicon, and Iron.**

One of the readiest means of opening out the alloy for the estimation of any one of these constituents is by fusion with acid potassium sulphate. Fuse about 10 grams of this salt in a capacious platinum crucible, allow it to solidify, and over the surface sprinkle half a gram of the powdered alloy. Heat over a bunsen flame until no gritty particles can be felt with a stout platinum wire. Leave the wire to cool with the fused mass, so that on digesting with water the whole may be lifted from the crucible. Add about 10 c.c. of sulphuric acid and heat gently until all but the silica has passed into solution. The silica is filtered off, ignited, treated with hydrofluoric acid, the loss in weight calculated to silicon, and the residue re-heated with sulphuric acid, and added to the main solution.

After making the main solution up to a definite volume, a fraction of it is reduced with sulphurous acid and titrated with permanganate for the estimation of the iron.

The remainder of the solution is neutralized, made slightly acid

again, boiled with thiosulphate, etc., as in the estimation of titanium in steels (page 96). The ignited titanic oxide may contain aluminium, which is separated and, if necessary, estimated as on page 123.

For these estimations the alloy may also be opened out with nitro-hydrochloric acid, 15 c.c. of sulphuric acid (per gram of alloy) being afterwards added. After evaporation to appearance of sulphur trioxide fumes, the mass is allowed to cool, a few c.c. of hydrochloric acid added, then about 100 c.c. water, and the whole boiled until the solution is cleared. The silica is filtered off and estimated as before, and the filtrate, as previously, is used for the other estimations, except that, as hydrochloric acid is present, the reduced iron solution is titrated with bichromate instead of permanganate.

### Phosphorus.

The alloy (one gram) is fused with a mixture of sodium carbonate and potassium nitrate, the cooled melt digested with water and filtered. The filtrate is acidified, and may now be tested for aluminium by adding a small excess of ammonium hydrate so as to decide whether it is advisable to make the aluminium-titanium separation mentioned above. In any case re-acidify and add a decigram of pure iron dissolved in nitric acid, and then make the mixture slightly alkaline again with ammonia. Collect the precipitated ferric hydrate which contains the phosphorus, dissolve it in nitric acid, make the solution just neutral (*i.e.* to the appearance of the red colour), add 30 c.c. of the nitro-molybdate reagent, and finish the estimation as usual.

Very small amounts of titanium interfere with the estimation of phosphorus in iron and steel. If the acid solution is evaporated to dryness, a portion of the titanium remains with the residue, after treatment with hydrochloric acid, as a phospho-titanate of iron; but unless sufficient phosphorus is present to keep it all in that condition, a portion also passes into solution. Provision is always made to avoid the error due to the formation of phospho-titanate, but generally the titanium which passes into solution is ignored altogether, on the assumption that it exercises no influence either on the precipitation or estimation of ammonium phospho-molybdate. In fact an example could be cited of a process specially recommended for titaniferous material, in which all the titanium is made to pass into solution. Now Pattinson has shown (*Journ. Soc. Chem. Ind.* 1895, 443 and 1022) that titanium in solution very seriously retards, and may altogether

prevent, the formation of the phospho-molybdate, and he gives the following very instructive table :

Approximate Volume of Liquid.	Tempera- ture.	Weight of Phospho- Molybdate Equivalent to Phosphorus taken.	Weight of Titanic Oxide in Solution.	Weight of Phospho-Molybdate formed.
		Grams.	Grams.	Grams.
70 c.c.	85° C.	0·122	0·114	none
"	"	"	0·016	trace
"	"	"	0·008	0·071
40 c.c.	"	0·140	0·016	0·103
"	"	"	0·008	0·118
70 c.c.	107° C.	0·122	0·016	0·088
"	"	"	0·008	0·110
40 c.c.	"	0·140	0·016	0·118
"	"	"	0·008	0·122

Pattinson suggests the following method for estimating phosphorus in titaniferous ores and irons :

The usual amount of the sample is dissolved in 1·20 nitric acid, evaporated to dryness, and taken up with hydrochloric acid. Without filtering, the ferric chloride solution is then reduced to the ferrous state by means of sulphurous acid, and sufficient alum added to combine with all the phosphoric acid. The basic phosphate of aluminium is now precipitated either with a slight excess of ammonia or with calcium carbonate. The resulting precipitate is fused with sodium carbonate, the mass digested with water, and any oxide of iron or sodium titanate filtered off. The phosphorus in the filtrate may be collected by adding a little ferric chloride, precipitating as ferric phosphate, dissolving the precipitate in nitric acid, and estimating *viâ* the nitro-molybdate reagent in the usual manner as lead molybdate.

The advantage of precipitating a basic phosphate of aluminium instead of the iron compound, lies in the fact that the former compound readily dissolves in fused sodium carbonate, and the fused mass is completely soluble in water ; whereas, in order to completely decompose a basic ferric phosphate, a second, and sometimes even a third fusion may be necessary.

TYPICAL ANALYSES.

Carbon, - - -	0·20	0·32
Silicon, - - -	2·89	1·06
Manganese, - - -	0·60	0·75
Sulphur, - - -	0·014	0·06
Phosphorus, - - -	0·064	0·12
Titanium, - - -	28·00	34·62
Iron, - - -	67·20	61·28
Aluminium, - - -	1·00	1·48
	99·968	99·69

## **ALUMINIUM ALLOYS.**

### **FERRO-ALUMINIUM.**

#### **Carbon.**

Aluminium behaves like silicon in its effect on the carbon; these alloys therefore always contain graphite. Total carbon is determined by separating iron and aluminium with a solution of the double copper salt, and burning the residue to carbon dioxide in the usual way.

#### **Silicon.**

See estimation of sulphur; also estimation of silicon in Metallic Aluminium.

#### **Manganese.**

Use the red lead or bismuthate process as for steels. Decomposition of sample is assisted by a few c.c.'s hydrofluoric acid if necessary.

#### **Sulphur.**

Aqua regia and barium sulphate process as for steels. The silicon may be determined on the insoluble residue.

#### **Phosphorus.**

This element is determined as in Pig-irons.

#### **Aluminium.**

The filtrate from the silica is made up to a definite volume or a special sample dissolved in hydrochloric acid, and so much measured out as represents a half to one gram of the alloy according to its supposed richness in aluminium. If about a decigram of aluminium is present proceed as follows: if more it is only necessary to add larger amounts of sodium phosphate.

To the acid solution add two grams of sodium phosphate, and ammonia until a small permanent precipitate forms: then clear the solution with hydrochloric acid and add one or two c.c. in excess. Heat to boiling, dilute to about 300 c.c. with hot water, add ten grams of thiosulphate in excess of the amount necessary to reduce any ferric iron, and then 20 c.c. acetic acid. Boil for fifteen minutes, filter, wash by decantation with boiling water containing a mere trace of ammonium phosphate, and ignite. Re-dissolve the ignited precipitate in hydrochloric acid, filter off any insoluble matter, and re-precipitate as before after adding one gram of sodium phosphate.

The quantitative precipitation of alumina by boiling neutral solutions with thiosulphate is accredited to Wöhler. Whenever phosphoric acid is present, however, it is always partly precipitated along with the alumina, and it is therefore best to avoid this error by precipitating at once as the normal phosphate. More than enough thiosulphate to decompose all free mineral acid must always be present, and so too must considerably more phosphoric acid than is required to form aluminium phosphate.

We have made a large number of determinations by the above method on solutions containing a decigram of aluminium and varying excesses of concentrated hydrochloric acid up to 7 c.c. We may quote one series where an excess of 3 c.c. hydrochloric acid was added after the ammonia precipitate had been cleared up.

- |   |         |
|---|---------|
| i. First precipitation : $\text{AlPO}_4$ obtained, - - -  | 0.4480. |
| ii. Re-dissolved (i) and re-precipitated exactly as before, but added only one gram sod. phosphate, - | 0.4490. |
| iii. Re-precipitated (ii), but added no phosphate, -  | 0.4220. |
| iv. Re-precipitated (iii) as in (ii), - - -   | 0.4485. |

These results show that in the presence of the theoretical amount of phosphoric acid the precipitate is not the normal phosphate but a basic compound, which, nevertheless, contains all the alumina.

## METALLIC ALUMINIUM.

### Carbon.

Aluminium acts very energetically with cuprammonium chloride solution ; it should therefore be added in very coarse borings or even as a single piece, and the carbonaceous residue collected and burned as usual. Regelsberger (*Journ. Soc. Chem. Ind.*, 1891, 1034), estimates the carbon by direct wet oxidation with chromic and sulphuric acids.

### Silicon.

Two interesting facts about this estimation are : that a portion of the silicon exists in the graphitic state ; and an appreciable amount of silicuretted hydrogen escapes when the metal is dissolved in hydrochloric acid. Sibbers found that by operating in a closed flask in a current of hydrogen and igniting the issuing gas, the escaping silica was deposited.

Although attention has been repeatedly drawn to the latter of the first

mentioned facts, hydrochloric is still used alone for decomposing the metal. The better plan is to dissolve three grams of the sample with nitro-hydrochloric acid, and evaporate with 15-20 c.c. sulphuric acid until the mass fumes. Water and a small amount of hydrochloric acid are then added and the solution boiled until only a siliceous residue remains, and filtered. The brownish-grey residue may contain small amounts of aluminium, copper, carbon, and iron, besides silicon and silica.

*The Total Silicon*, if that only is required, is obtained by fusing the residue with sodium carbonate, evaporating the dissolved melt with hydrochloric or sulphuric acid, and collecting the silica and determining its weight in the usual manner.

*Both Graphitic and Combined Silicon* may, however, be separately estimated. By treating the residue with hydrofluoric and a drop of sulphuric acids, the loss in weight gives the silica equivalent to the silicon existing in the combined state. The unattacked residue, which is now much darker in colour, is treated in the same manner with a mixture of hydrofluoric and nitric acids: the loss in weight now represents graphitic silicon. The results are not quite accurate, because the graphitic silicon is slightly oxidized by the treatment for driving off the silica.

*The Graphitic Silicon* only is determined by dissolving the aluminium in a mixture of hydrochloric and hydrofluoric acids, filtering through a paraffin coated funnel, and treating the ignited residue either by fusion or at once with nitro-fluoric acid (Handy).

#### **Manganese, Sulphur, and Phosphorus.**

These elements occur generally in quite negligible amounts only. They may be determined as in ferro-aluminium.

Noaillon has observed that the influence of aluminium chloride on the results obtained by using the barium-sulphate process for estimating sulphur is opposite to that exerted by ferric chloride, *i.e.* the results tend to be above rather than below the truth. This he thinks is due to the co-precipitation of aluminium chloride. The error becomes very slight when precipitation is made from solutions containing five per cent. hydrochloric acid, and the precipitate is more easily handled.

Gouthiere estimates sulphur by heating the metal to redness in a current of two-thirds hydrogen and one-third carbon dioxide gas (Rollet's process), passing the evolved sulphuretted hydrogen into silver nitrate, and weighing the precipitated sulphide.



### Iron.

To the filtrate from the silicon estimation including the small amount of ferric oxide remaining after volatilizing the silica, add caustic soda until the precipitated alumina re-dissolves. Dilute the solution to 300-400 c.c., and allow to stand an hour or two in a warm place. Filter, wash, dissolve the precipitate in dilute acid, reduce to the ferrous state, and titrate with bichromate or permanganate.

If a separate sample must be taken, dissolve ten grams of caustic soda in about 150 c.c. water and add two grams of the metal. Filter off the precipitated ferrous hydrate and proceed as above. This mode of effecting decomposition (in a nickel basin), followed by evaporation with hydrochloric acid (after transferring to a porcelain dish), can be conveniently used for the estimation of total silicon.

### Copper.

Dissolve five grams of the metal in hydrochloric acid, filter off the insoluble residue, ignite it, add hydrofluoric, nitric, and sulphuric acids, and evaporate until the two former are driven off. Dilute the sulphuric acid residue, add it to the main filtrate, and pass sulphuretted hydrogen or add a few grams of sodium thiosulphate. Collect the precipitated sulphide of copper, ignite it to oxide, and estimate the copper either gravimetrically or volumetrically as in steel.

### Sodium.

This element has a very deleterious influence on the physical properties of aluminium. In some cases it is possible to extract a portion of the sodium simply by digesting with water. The following process (Moissan's) depends on the fact that aluminium nitrate is decomposed by heating, yielding alumina, at a much lower temperature than sodium nitrate.

Dissolve five grams of the metal in strong nitric acid diluted with an equal bulk of water, raising the temperature carefully so that the evolution of gas may not be too violent. Concentrate the solution in a platinum dish and bring the dry residue to a powdery state with an agate pestle. Heat the dried residue below the fusion point of sodium nitrate until all nitrous vapours are driven off; then digest with boiling water, decant the liquid, and wash the alumina three or four times.

The filtrate and washings are again evaporated to dryness with a few drops of nitric acid and the residue dissolved in boiling water, any

alumina being filtered off. The solution is now evaporated with hydrochloric acid and heated to 300° C. The sodium chloride remaining is determined as silver chloride and calculated to sodium.

Some chemists determine the sodium by what is essentially the Lawrence-Smith process for alkalis (page 216).

Aluminium.

A direct determination of the aluminium may be made by the process used for ferro-aluminium ; but—assuming a complete analysis is being made—the result is not likely to be nearer the truth than if estimated by difference. It is a difficult matter to obtain, and operate with, perfectly dehydrated alumina or its phosphate.

Other Constituents.

Aluminium also contains a small amount of nitrogen, which is evolved (and estimated) as ammonia when the metal is dissolved in caustic potash : it is probably present as nitride.

The commercial metal may also contain small amounts of amorphous alumina and sometimes small crystals of carbon boride (Moissan). Very refined analysis has also shown the presence of potassium, calcium, silver, lead, gallium, and indium, but in such small amounts as not to affect the known properties of the metal.

Aluminium is alloyed for various purposes with copper, nickel, manganese, chromium, tungsten, titanium, zinc, cadmium, tin, etc. ; but none of these alloys are common to steel-works practice. Aluminium bronze is dealt with on p. 270.

TYPICAL ANALYSES.

	Aluminium.		Ferro-Aluminium.	
Carbon, - - -	0·04	0·41	2·65	1·75
Silicon (total), - -	1·78	0·15	1·65	2·36
„ (graphitic), - -	0·40	—	—	—
Manganese, - - -	0·01	—	0·58	0·79
Sulphur, - - -	—	—	0·10	0·05
Phosphorus, - - -	traces	—	1·30	0·24
Copper, - - -	0·01	0·35	—	0·10
Sodium, - - -	—	0·10	—	—
Iron, - - -	0·80	0·27	84·28	70·41
Aluminium, - - -	97·36	98·72	9·40	24·14
	100·00	100·00	99·96	99·84

**FERRO-BORON.**

The use of this alloy does not appear to have got beyond the experimental stage. No methods have been specially devised for the determination of boron in iron compounds, but one of a kind most acceptable to steel-works analysts could probably be worked out from the observation of E. S. Smith (*Chem. News*, xlv. 286):

“When a solution of manganous sulphate is added to one of borax, and to this mixture an equal volume of alcohol a white flocculent precipitate of manganese borate ( $\text{MnB}_4\text{O}_7$ ) which is insoluble in the alcoholic liquid, rapidly separates. The excess of manganous sulphate remains in solution, and can be readily determined in the filtrate from the borate after expelling alcohol.” A series of very satisfactory test analyses is given.

A modification of the above process, which is said to give good results, has been proposed by Carnielli (*Journ. Chem. Soc.*, lxxx. ii. 690).

According to Warren (*Chem. News*, lxviii. 200) buttons obtained in the dry assay of iron with a borax flux may contain one or two per cent. of boron.

## PART IV. RAPID ANALYSIS AT THE FURNACE.

IN making large castings of special steel, armour plates for instance, the percentage of a number of elements must be determined while the metal is still in the furnace, in order that the amount of alloy to make up the required percentage of this or that constituent may be added. In some cases this information cannot be deduced even approximately from any striking physical property of the metal, and so it is becoming more and more a common thing to be called upon to estimate with tolerable accuracy, and in a few minutes, the percentage of carbon, nickel, chromium, etc. The object of this section is to describe such processes as are in use and seem best able to meet this demand.

### CARBON.

The percentage of this element is controlled by the Eggertz colour test and the "fracture" of small spoon samples. The spoonful of metal is cooled,<sup>1</sup> broken so that the fracture may be observed, drilled, and one or two decigrams of sievings weighed off along with a standard steel of similar material which has been treated in the same way. After adding a measured amount (5 c.c.) of hot 1.20 nitric acid the test tubes are pushed in a sand-bath or placed in a paraffin bath at 135° C. In from two to three minutes the solutions are rapidly cooled, transferred to graduated tubes, and matched as usual. The remarkable speed attainable and the comparative accuracy are surprising. When suitably chosen test tubes are used the colours are often compared by the practised eye without transferring to graduated tubes.

### SILICON.

The following is Ford's method for estimating silicon in molten pig-metal when it is being taken directly from the furnace to the con-

<sup>1</sup> Sometimes in soapy water to assist subsequent drilling.

verter—the information is generally required as a guide in blowing the metal :

The sample is taken in a small ladle as the iron runs from the furnace. The ladle is then held about three feet above a bucket of water and given a circular motion as the molten metal is being poured. This causes the iron to form in globules more or less round, according to the amount of silicon it contains. Thus with iron containing two per cent. of silicon or more, the globules will be almost perfectly round, concave on the upper surface, and generally from a quarter inch (6 mm.) to three eighths inch (9 mm.) in diameter. If the iron is low in silicon, the shot will be small, flat, and irregular in shape ; while if the iron be very low, as is the case with spiegel and ferro-manganese, the shot will be elongated and have tails sometimes quarter of an inch long. A careful observer can soon judge the amount of silicon very closely from the condition of the shot.

Take the shot from the bucket and place in the hot ladle, where they dry instantly. Then crush in a steel mortar, weigh off half a gram of the fine sievings into a platinum dish, add 10 c.c. hydrochloric acid (1.2 spec. grav.), and cover with a watch glass. When the iron is dissolved evaporate over a naked flame as rapidly as possible. As soon as dry, add dilute hydrochloric acid to the hot dish, boil until any ferric oxide (which may have been formed by decomposition of the chloride) is dissolved, dilute and filter. Ignite the precipitate in a weighed platinum crucible over a blast lamp and gently direct a small jet of oxygen on to it as soon as the paper is burned off. Then cool the crucible, weigh, and calculate the silicon.

Results are obtained by this method in twelve minutes from the time the ladle is put into the molten iron, and they are accurate enough for practical purposes.

## MANGANESE.

The estimation of this element is not generally required. If it were, no doubt the bismuthate process could be suited to the occasion. The following speed test, made by an expert operator and timed by one of the authors, shows what could be done if necessary :

Borings received, -	-	-	-	-	-	12.10 A.M.
Weighed and dissolved,	-	-	-	-	-	12.14
Cooled,	-	-	-	-	-	12.15½
Oxidized and filtered,	-	-	-	-	-	12.17½
Result, -	-	-	-	-	-	12.18½

## PHOSPHORUS.

The oxidation of phosphorus in the basic process is controlled by casting a sample always in the same sized mould, and after solidification hammering flat and quenching. The presence of large amounts of phosphorus give the fracture a bright crystalline and characteristic streaky appearance. Some practical steel makers maintain that if the test piece is always prepared in the same manner, the amount of phosphorus can be estimated by the fracture to a few hundredths per cent.

Galbraith proposes to supplement the above test in the following manner. Dissolve two decigrams of the sample in aqua regia, add 3 c.c. water, enough ammonia to precipitate the iron, enough nitric acid to re-dissolve it, and then ten drops of the molybdate reagent. The turbidity, due to precipitated phospho-molybdate, is compared with that in a steel solution containing a known amount of phosphorus. The comparison is made after shaking in small stoppered bottles half an inch wide.

Persons making regular determinations in the laboratory on two grams of the material can judge the percentage phosphorus from the precipitated phospho-molybdate with fair accuracy. It is claimed (Mahon) that, besides being formed, this precipitate can be filtered off, washed, dissolved in caustic soda, and titrated with standard acid in eight minutes.

## CHROMIUM.

The following process has been in regular use for examining molten steel intended for the manufacture of armour-piercing projectiles :

Dissolve three decigrams of fine drillings in 8 c.c. dilute sulphuric acid (1 to 3) in wide test tubes or small beakers, and heat on a small sand bath until dissolved. Filter and compare the filtrate with a standard as in the carbon colour test.

Ferrous sulphate has a green, though of course much fainter colour than chromic sulphate, and as the standard and sample diverge from each other it becomes increasingly desirable to make a correction for it. In furnace practice, however, an abundance of suitable standards may always be had.

Mr. T. W. Hogg finds that determinations of chromium made in the laboratory in this way give results which compare very concordantly with those obtained by more elaborate processes.

**NICKEL.**

This element may be estimated in two ways, both of which depend on a reaction already fully dealt with, viz. titration with cyanide of potassium and silver nitrate.

**1. Without Separating the Iron.**

Weigh off one gram of the sample and add 10 c.c. hydrochloric acid, diluted with an equal bulk of hot water; when it is at least mainly dissolved add 10 c.c. 1·20 nitric acid. Cool the solution, add 3 grams of citric acid, two grams of ammonium sulphate, and as much dilute ammonia as will make the solution slightly but distinctly alkaline (about 80 c.c. of binormal strength). Add 2 c.c. of a two per cent. potassium iodide solution, and as much silver nitrate as forms an obvious turbidity. Run in potassium cyanide from a burette until the turbidity just disappears.

The nickel is calculated from the volume of cyanide used after deducting the amount needed to clear the same quantity of silver nitrate and potassium iodide when titrated alone. The cyanide is standardized as before, or, if preferred, under conditions identical with those of the estimation.

Alkaline citrate solutions of iron are of course very dark coloured, and small variations in the turbidity are not easy to follow in the ordinary manner. The difficulty is greatly lessened by performing the operation in the shade and arranging a strong beam of light to cross the liquid. So long as the solution is turbid the path of the light is very distinct; as soon as the turbidity disappears the beam of light is hardly visible, except as it falls on small air bubbles caused by the shaking. A suitable beam of light is provided by enclosing an electric lamp in a box fitted with a condensing lens.

The chief drawback to this process lies in the fact that when chromium is present the silver iodide turbidity will disappear when considerably less potassium cyanide has been added than is required to form the double cyanide with the nickel present; but it recurs again and again. This recurring turbidity not only delays the process, but also leaves the mind somewhat undecided as to when the final point has really been reached.

The following process is not influenced by the presence of chromium, and it may be worked through in ten minutes or less when everything has been prepared beforehand:

## 2. Separating the Iron and Chromium.

Dissolve the sample as before, pour into a half litre flask already partly filled with cold water, and containing also nearly half the 70 c.c. binormal ammonia which is to be used for precipitating the iron. Run in an excess of cyanide from a burette and add the remaining portion of ammonia, which should be sufficient to precipitate all the iron, and leave the filtered solution suitably alkaline for the subsequent titration. Make up to 500 c.c., mix well, and filter 250 c.c. through a fluted paper. During filtration add 2 c.c. potassium iodide solution and a little ammonium sulphate to a clean flask, empty the filtered solution into this, and add silver nitrate from a burette until a turbidity appears.

If 5.79 grams of silver nitrate are dissolved in a litre of water, each cubic centimetre of the solution is equivalent to 0.001 gram nickel, or equal to a tenth per cent. nickel if one gram of the steel is used. The potassium cyanide and silver nitrate should be of equal strength, or their relative strengths known. In the former case the percentage of nickel in the steel is at once found by deducting twice the amount of silver nitrate used from the amount of cyanide added and dividing by ten.

Rather more cyanide must be added than is required to combine with the expected amount of nickel. In making furnace tests the amount of nickel present is known to within half per cent. or so. But supposing it were otherwise, is there any disadvantage in using larger excesses of cyanide than are required? To answer this question a series of results were obtained by operating with similar amounts of a one per cent. nickel steel, and adding varying excesses of potassium cyanide. The cyanide required theoretically was 10 c.c.

KCN added.	Per cent. Nickel.	Per cent. Nickel Corrected.
13.3 c.c.	1.01	1.00
16.0 c.c.	1.02	0.99
18.9 c.c.	1.05	1.01
22.8 c.c.	1.06	1.00
27.0 c.c.	1.06	0.98
32.5 c.c.	1.11	1.01

Large excesses of potassium cyanide, it is seen, cause high results. This is due to a portion of the cyanide combining with the iron as ferri-cyanide. This error, however, causes no serious inconvenience,



because when a large amount of silver nitrate was required to form the turbidity it would be known that the calculated result was too great. Happily the error is fairly proportionate, as may be seen from the third column of the table, where a correction has been made by increasing the amount of silver nitrate actually needed to destroy the excess of cyanide by five per cent.

The process is suitable for regular laboratory use, and is as exact as any other known if a preliminary test is made when the approximate percentage of nickel is uncertain.

### **TUNGSTEN.**

A mechanical means of detecting tungsten, suggested by Langley, may be fittingly placed here. On an emery wheel a tungsten steel gives only a dull fire free from exploding sparks, instead of the brilliant shower of sparks obtained from ordinary steels. Steels containing less than a half per cent. tungsten are said to be distinguished in this way.

## PART V. THE ANALYSIS OF ORES.

### IRON ORES.

THE ores of iron are either ferric oxide (hydrated or anhydrous), ferrous oxide, or carbonate, or mixtures of these with varying amounts of impurities. The chief impurities are compounds of silicon, manganese, sulphur, phosphorus, aluminium, calcium, magnesium, titanium, hydrogen, and carbon. Rarer impurities are barium, nickel, zinc, chromium, molybdenum, arsenic, copper, lead, and the alkalis. There are frequently present also traces of such rare elements as niobium, indium, gallium, etc., which may be detected spectroscopically, but may not be estimated or even detected by ordinary chemical analysis.

When a constituent of an ore may be estimated singly and directly, as the corresponding element is in the metal, the practice should be adopted. In this way a special determination can be made for any particular purpose, and in a complete examination the errors of analysis are more likely to be detected than when the estimations are preceded by a long series of separations on the same sample. Such series of separations even when badly made may allow the total to be very near that narcotic to a doubting mind—100·00 per cent.

#### Dissolving Ores.

All commercial ores leave a residue of more or less impure silica when heated with hydrochloric acid. When the residue is obviously impure, and particularly if it contains considerable iron, it must be further opened out before the analysis is proceeded with. This may be done by fusing with sodium carbonate or bisulphate, or sometimes by treating with hydrofluoric and sulphuric acids, and then finally mixing with the soluble portion. In some cases the insoluble residue is reported as 'crude silica,' and in some others it is analyzed and stated separately. In Percy's "Tables of Analysis of British Iron Ores" (*Iron and Steel*, p. 204) the latter mode is followed, and indeed there may be some advan-

tage in it from a purely scientific point of view ; but little, we think, from a works analyst's standpoint.

Crystalline ferric oxide—i.e. specular ore—though easily crushed to small laminae, is not easily ground so finely as to be quite soluble in acids. The glistening of small plates is apparent when a moderate amount of patience has been exhausted in grinding enough of the ore for a complete analysis. These ores may often be opened up as follows in a much more satisfactory manner than by fusion.

Pass the ore through a sieve of at least 90 meshes to the inch. Boil a weighed amount with strong hydrochloric acid and then dilute with some soft ashless paper which has been shaken to a pulp in water. Pour this mixture on to a pulp filter with constant agitation, and wash. The filter, which is now uniformly grey owing to the thorough dissemination of the small crystals, is transferred to a crucible, dried, and then charred at the muffle's mouth. The crystalline ferric oxide is reduced by the glowing mass of carbonized paper, and again re-oxidized when the paper is burned off and the crucible more strongly heated. Everything now passes into solution on heating with hydrochloric acid except a little silica.

From 12 to 14 c.c. concentrated hydrochloric acid will comfortably dissolve a gram of ore ; half that amount should be taken for each additional gram.

The following descriptions may be taken to apply to all kinds of ore after they have been suitably dissolved. They are conveniently abbreviated because so many of the operations are similar to those used in analyzing metals.

#### Moisture.

As consignments of ore may pick up considerable moisture en route from rain and snow storms, they should be brought to a definite hygroscopic state, in order that results may be comparable, whether an exact determination of the moisture is required or not. To make the operation quantitative break the ore to pea-sized pieces and weigh off twenty to fifty grams, heat for several hours at 105° C., and re-weigh.

After grinding and passing through a sixty or ninety-mesh sieve the ore should be kept in a stoppered bottle.

#### Total Iron.

If the ore contains carbonaceous matter one gram of it is roasted in the muffle before being heated with hydrochloric acid.

With familiar ores the siliceous residue may be neglected when apparently free from iron ; but otherwise they should be fused or treated

with hydrofluoric and sulphuric acids and such iron as may have existed as colourless compounds looked for, and if found added to the bulk.

The ferric solution is then nearly neutralized with ammonia, reduced by an excess of sulphurous acid, re-acidified, the sulphur dioxide boiled off, and the somewhat cooled solution titrated with decinormal bichromate.

Where valuation of ores is the order of the day it is no doubt quicker to perform the reduction with stannous chloride in strongly acidified solutions, but as we have no practical experience of this simple method the interested reader must consult the Bibliography, and look up details for himself. Different modifications of the process are described in the well-known books written respectively by Sutton, Blair, Lord, Fresenius, Dittmar, and Ledebur, as well as in others less-known and accessible.

### **Ferrous Oxide.**

This constituent can be satisfactorily determined only when the ore is free from higher oxides of manganese and organic matter. The former would evolve chlorine with hydrochloric acid, and so cause the results to be low; the latter, by reacting with the bichromate or permanganate used, might make the results too high. It is sometimes possible in the presence of organic matter to estimate the ferrous oxide approximately, after dissolving as usual and cooling, if the organic matter is removed before titrating. Sometimes also a similarly questionable result may be obtained by titrating the iron existing in the ferric state with stannous chloride and iodine; the ferrous oxide being then found by difference after determining the total iron. The presence of pyrites would of course interfere with an accurate estimation.

The direct determination is made as follows: Place one gram of the ore along with a good pinch of sodium bicarbonate into a flask fitted like the one used for standardizing permanganate (page 108) and add 20 c.c. hot hydrochloric acid. When the ore is quite decomposed, cool and dilute. If a spot test with ferri-cyanide shows that ferrous oxide is present, titrate with bichromate.

$$1 \text{ c.c. } \frac{N}{10} \text{ K}_2\text{Cr}_2\text{O}_7 = 0.0072 \text{ gram FeO.}$$

The ferrous oxide in insoluble residues is assayed separately as in refractory materials.

### **Silica, Alumina, and Titanic Oxide.**

Decompose from three to five grams of the well-ground ore with hydrochloric acid and boil to dryness. 'Take up' in hydrochloric acid

and collect, ignite, and weigh the silica. If the silica is tolerably pure, determine its amount by volatilization with hydrofluoric acid, and add the ignited residue after dissolving (*via* fusion if necessary) to the filtrate.

Alumina is precipitated from the ferric solution by adding two or three grams of sodium phosphate, adjusting the acidity, reducing the iron to the ferrous state with thiosulphate, precipitating aluminium phosphate with an excess of the same salt, and completing the estimation as in steel or ferro-aluminium.

Any titanitic oxide existing in the ore will be found with the aluminium phosphate in a form closely approximating to  $\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ , and according to its amount it can be estimated colorimetrically or gravimetrically in the already described ways.

If titanitic oxide only is being looked for, the dissolved ore is evaporated with sulphuric acid, the siliceous residue dissolved in hydrofluoric and sulphuric acid and evaporated to strong fumes, the two solutions mixed, and hydrogen peroxide added as usual. A gravimetric estimation necessarily involves the precipitation of alumina and titanitic oxide together and their separation as on page 123.

#### Manganese.

Some ores go completely into solution on digesting in a platinum crucible with a mixture of hydrofluoric and nitric acids, and the bismuthate process can then be applied at once after diluting and boiling; but this mode of attack often fails or is troublesome.

The following is a more general process: Dissolve one gram of the ore in hydrochloric acid, add a little hydrofluoric acid if the siliceous residue is considerable, then 10 c.c. sulphuric acid, and evaporate until the solution fumes strongly, so as to completely expel all chlorides. Transfer from the porcelain dish to a flask, dilute with an equal volume of water, add 30 c.c. 1·20 nitric acid, and if everything is dissolved, cool, add an excess of bismuthate, and finish as usual.

$$1 \text{ c.c. } \frac{N}{10} \text{ KMnO}_4 = 0\cdot00142 \text{ gram MnO.}$$

#### Sulphur.

This element may exist as sulphide (pyrites, galena) or sulphate (gypsum, barytes).

Five to ten grams of an ordinary ore are digested with nitro-hydrochloric acid, and the soluble portion, after evaporation, treated as though it were a steel. To examine the insoluble portion, fuse with sodium

carbonate, extract the melt with water, filter, or filter a fraction only if the residue is considerable, acidify, evaporate to dryness or not to remove silica according as the solution remains clear or becomes turbid, and finally precipitate with barium chloride and weigh the sulphate. Detailed instructions for the estimation of sulphur in ores containing barium are given on page 203.

### Phosphorus.

In dealing with strange ores the most important consideration by far in relation to the estimation of phosphorus is whether or not the ore contains titanitic oxide. It is well therefore to postpone this determination until the alumina has been done and the presence or absence of titanium settled.

(a) *If Titanium is present* dissolve two grams of the ore in hydrochloric acid, eliminate silica from the separated residue with hydrofluoric and sulphuric acids, mix the two solutions, reduce the iron to the ferrous state, add alum, collect the phosphorus in the form of basic aluminium phosphate, and go through the remaining operations as on page 173.

(b) *If Titanium is absent* dissolve two grams of the ore in hydrochloric acid, evaporate nearly to dryness, add 50 c.c. 1.20 nitric acid, and then while vigorously boiling add a strong solution of permanganate in small portions at a time until a persistent precipitate of manganic oxide forms. As much hydrochloric acid as possible should be evaporated in the first instance, providing only the added nitric acid can form a clear solution; the remaining hydrochloric acid is then quickly eliminated.

The nitric acid solution of the ore is cleared with a few drops of sulphurous acid, filtered, washed with very little water, ammonia added until there are signs of ferric oxy-compounds forming, i.e. until the solution becomes a much deeper red in colour, and then precipitated with the nitro-molybdate reagent, and finished as usual.

Any phosphorus which it is feared may exist in the residue can be easily detected by treating with hydrofluoric and sulphuric acids, and testing the evaporated solution with molybdate.

We have never seen a nitro-molybdate solution made to any formula whatever, except such as contained organic acids, which did not deposit molybdic oxide after a few weeks or months. When so little demand exists that the solution becomes considerably weakened in this way before the quantity made can be used up, it is better to keep a solution of ammonium molybdate and add nitric acid to as much of it as is needed. Thus, a hundred grams of molybdic oxide may be dissolved

in 70 c.c. strong ammonia, and made up to 200 c.c. Ten c.c. of this solution mixed with 30 c.c. 1.20 nitric acid are equal to 40 c.c. of the mixture recommended on page 56.

The separate addition to the steel solution in proportionate amounts of nitric acid and alkaline ammonium molybdate should not be practised. The results thus obtained are always too high through occlusion by the precipitate of extra molybdic oxide. With tap cinders and basic slags results two or three per cent. too high have been obtained in this way.

### Carbon Dioxide.

The amount of this constituent may be very considerable, but its influence in works' operations is relatively small, and consequently the almost universal mode of determining it is by loss when the ore is treated with acid. Any of the more perfected and elaborate pieces of apparatus figured in trade catalogues may be used, but a simple form, such as Parnell's, Fresenius and Wills', or the one shown in Fig. 13, meets most requirements.

From one to two grams of the ore is weighed into the small tube *A*, which is made by cutting down a test tube and flattening the bottom. About 20 c.c. dilute sulphuric acid is added to the flask and the small tube arranged so that no acid can touch the ore. The complete apparatus is then weighed. The ore and acid may be brought into contact, and the liberation of carbon dioxide controlled somewhat by gently tapping and shaking the flask. When all action has ceased the mixture is warmed, but by no means boiled, and a stream of dry air aspirated through the solution and the upright calcium chloride tube so as to drive out carbon dioxide, but no moisture. The flask is allowed to stand, having its entrance and exit closed with rubber caps, until it is quite cold, then re-weighed, and the loss calculated to percentage.

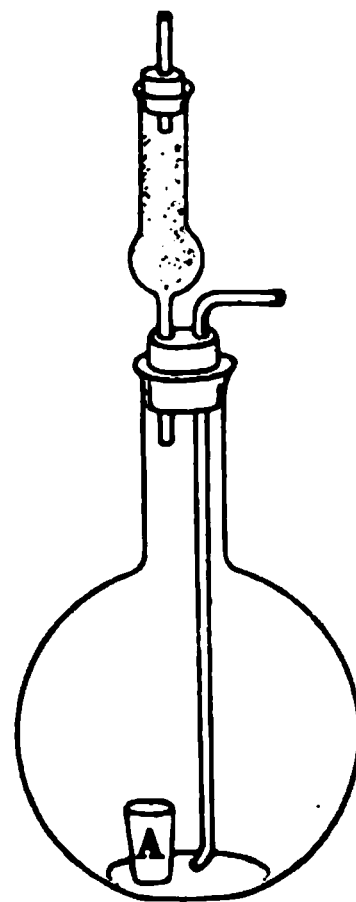


FIG. 13.

A direct estimation can be made by attaching a weighed potash bulb to the calcium chloride tube so as to absorb the evolved carbon dioxide.

### Water and Organic Matter.

If an ore is free from carbon dioxide and ferrous oxide, it is generally sufficiently accurate to express these constituents as "Loss on Ignition." The limited practice of making an analysis add up to a hundred

per cent. by calling the difference water and organic matter is less commendable.

Both constituents may be estimated together or separately, as in manganese ores on page 202; in the latter case a weighed calcium chloride tube must come between the combustion tube and the potash bulb.

#### **Lime and Magnesia.**

Dissolve three grams of the ore in a liberal amount of hydrochloric acid. If the residue is small and not likely to contain either of the constituents sought, the acid solution is neutralized with ammonia and ammonium carbonate without filtering. The solution is then diluted to about 250 c.c., and the iron precipitated with a few cubic centimetres ammonium acetate and two or three c.c. acetic acid. Heat the mixture to boiling, make up to about 305 c.c., and at once filter off 200 c.c. through a fluted paper. If large amounts of manganese are present, or nickel or copper, then make the filtrate decidedly alkaline, and precipitate with sulphuretted hydrogen. But if a small amount of manganese only is present, its precipitation with bromine and a small excess of ammonia causes no appreciable loss of either lime or magnesia.

Filter off the precipitated manganese, evaporate the solution to the limits of a 200 c.c. beaker, and precipitate the lime as oxalate, and weigh as oxide or sulphate.

The ammonium chloride which it is desirable to have present during each of the preceding separations, but which may prevent the final solution being evaporated to as low a bulk as is desirable for the precipitation of ammonium magnesium phosphate, is conveniently driven off by evaporating to low bulk with nitric acid.

#### **Chromium.**

Two grams of the ore are fused with sodium carbonate with free access of air in a platinum dish, or with sodium peroxide in a nickel crucible, and the fused mass extracted with water. A yellow filtrate indicates chromium. Its amount may be estimated colorimetrically by comparison with standard solutions of sodium chromate or by acidifying the filtrate with sulphuric acid, and titrating with permanganate.

$$1 \text{ c.c. } \frac{N}{10} \text{ KMnO}_4 = 0.00254 \text{ gram Cr}_2\text{O}_3.$$

If more than one or two tenths per cent. are present the ore is dissolved in hydrochloric acid and any insoluble residue also dissolved after fusion. The solution is then evaporated with sulphuric acid and treated as that of a steel.



**Vanadium.**

If titanium is absent the colour test for vanadium is applied by dissolving in hydrochloric acid, evaporating with sulphuric acid, and adding hydrogen peroxide. Its presence may also be detected by fusing with caustic soda in an open silver dish, extracting with water, and passing sulphuretted hydrogen through the filtrate. The reddish violet colour of the sulphovanadite is characteristic.

To estimate vanadium colorimetrically when titanium is also present the latter may be precipitated along with any aluminium and chromium by boiling faintly acidified solutions with thiosulphate. The filtrate is then boiled with nitric acid and evaporated with sulphuric acid so as to eliminate chlorides before adding hydrogen peroxide. The ignited residue must always be fused with sodium carbonate, the melt extracted with water, and vanadium looked for in the acidified solution.

As an alternative the vanadium may be precipitated from a solution of ten grams of the ore as a basic aluminium vanadate (page 92). The washed precipitate is fused, extracted with water, the acidified filtrate reduced with sulphurous acid and titrated with permanganate.

$$1 \text{ c.c. } \frac{N}{10} \text{ KMnO}_4 = 0.00912 \text{ gram V}_2\text{O}_5.$$

Special methods would be required for the rich vanadiferous ores used in the manufacture of ferro-vanadium, but a steel-works' demand for such processes does not at present exist.

**Copper, Zinc, Nickel, Cobalt.**

These constituents are present in British iron ores in negligible amounts only. To determine whether any or all the oxides are worth consideration, dissolve five grams of the ore in hydrochloric acid, and make an acetate separation. It is well to aim at making the neutralization so nicely that the ferric oxychloride is decomposed by boiling without adding any acetate, so that the filtrate may contain practically all the copper as well as the manganese, nickel, cobalt, and zinc.

Make the filtrate slightly ammoniacal, add 3 or 4 c.c. acetic acid and a few c.c. ammonium acetate, and pass sulphuretted hydrogen. The manganese only remains in solution. If the volume of the precipitate warrants a further examination dissolve it in nitric acid, evaporate to dryness, take up in hydrochloric acid, precipitate copper with sulphuretted hydrogen, and estimate its amount in the usual way.

Add sodium carbonate to the concentrated filtrate until a faint precipitate appears, clear with a drop of hydrochloric acid, and pass sulphuretted hydrogen. Any zinc sulphide precipitated is washed

with sulphuretted hydrogen water, and either ignited to oxide or transformed to phosphate. In the former case a re-ignition with ammonium carbonate is needed to completely expel sulphuric acid.

The filtrate containing nickel and cobalt is acidified, boiled to eliminate sulphuretted hydrogen, and the combined metals estimated cyanometrically.

When the approximate amounts of these rarely occurring oxides have been sorted out in the above fashion, the copper or nickel and cobalt may be estimated in a more direct way by dissolving ten grams of the ore, reducing the iron to the ferrous state, and passing sulphuretted hydrogen. The sulphide of copper is collected and ignited to oxide, or estimated iodometrically as in steel. The filtrate is then boiled, oxidized with nitric acid, the iron separated with acetate, and as large a fraction of the filtrate as convenient evaporated to a small bulk, and titrated with potassium cyanide and silver iodide.

### Zinc.

The method proposed by Hampe for the assay of zinc ores has been modified in the following way by Kinder (*Stahl und Eisen*, xvi. 675) so as to fit it for determining small amounts of zinc in iron ores.

Five grams of the ore are dissolved in hydrochloric and evaporated with sulphuric acid until the solution fumes. The cooled solution is diluted, digested, and filtered. The filtrate, which is now free from lead, is diluted to 300 or 400 c.c. and saturated with sulphuretted hydrogen. After removing copper sulphide, an excess of ammonium formate solution (made by neutralizing formic acid of 1.15 specific gravity with ammonia of 0.96 s.g.) and 15 c.c. formic acid is added. Any zinc present is precipitated as sulphide; but if the amount is considerable, more sulphuretted hydrogen should be passed into the warm solution.

If the precipitated zinc sulphide is white it may be at once weighed as such or as oxide; but if at all coloured it should be dissolved in hydrochloric acid, ammonia added to faintly alkaline reaction, then 15 c.c. excess of formic acid and the zinc re-precipitated as before.

We have had no experience with this method. See also Platz (*Journal Iron and Steel Inst.*, 1889, ii. 484), Flath (*Journ. Soc. Chem. Ind.* 1901, 935).

### Antimony and Lead.

These metals as well as arsenic would be precipitated along with copper in the operations described on page 193. Their separate estima-

tion need not be dealt with, as it proceeds on similar lines to those adopted in analyzing white metal alloys ; and, moreover, they are very rarely even looked for by the works' analyst. The former metal would be estimated with the arsenic in the second of the following methods :

#### Arsenic.

If the necessary apparatus is prepared the amount of arsenic in an ore is determined by simply dissolving a sample in the retort, then distilling with strong hydrochloric acid and ferrous chloride, and titrating the distillate.

To separate the arsenic so as to use the same mode of estimating it as is used for steels, a procedure described by Messrs. J. & H. S. Pattinson (*Jour. Soc. Chem. Ind.* 1898, 212) is very convenient, and, according to our test analyses, very accurate. As the separation is made in concentrated hydrochloric acid solutions, such amounts of lead, copper, and antimony as occur in iron or manganese ores do not interfere. Ordinary filter papers are apt to break with such acid solutions, and Messrs. Pattinson use asbestos : there is no difficulty, however, in using the paper *pulp* filter.

Dissolve three grams of the ore in 30 c.c. concentrated hydrochloric acid (and a little potassium chlorate or permanganate if the ore is likely to contain ferrous oxide) by gently heating. Filter the liquid through a small pulp filter and wash the residue two or three times with small amounts of strong hydrochloric acid. Add a strong solution of stannous chloride <sup>1</sup> until the disappearing colour shows that all the iron has been reduced to the ferrous state, and then one or two drops in excess.

The arsenic, now present as arsenious acid, is precipitated by saturating the cold liquid with sulphuretted hydrogen. The precipitated arsenious sulphide is collected on a small pulp filter and washed with a mixture of five parts hydrochloric acid and two parts sulphuretted hydrogen water, and finally with water alone. The filter is then split, treated with an excess of sodium sulphide and ammonium chloride to separate traces of iron, and the filtrate proceeded with **as** on page 105.

A process also devised by Messrs. J. & H. S. Pattinson (*Jour. Soc. Chem. Ind.* 1893, 119)<sup>2</sup> for eliminating arsenic during the estimation of phosphorus does not appear to be quite so simple and ready a means

<sup>1</sup> Made by dissolving fifty grams of pure tin, or its equivalent of stannous chloride, and afterwards diluting to 200 c.c. with strong hydrochloric acid.

<sup>2</sup> This paper deals with the influence of acidity, volume of solution, etc., on the precipitation of arsenic from ferrous solutions with zinc sulphide.

of separating arsenic as the foregoing, but our test analyses quite confirm those obtained gravimetrically by its authors.

Dissolve three grams of the ore as before and evaporate so as to leave only a very small excess of hydrochloric acid; a small siliceous residue need not be filtered off. Cool the solution, keep its volume below 50 c.c. and add a solution of thiosulphate (500 grams per litre) from a burette, until one drop fails to produce the violet colour of ferric thiosulphate. At the end of the reduction the solution should have no colour, or merely the green colour due to ferrous chloride. If only a small excess of hydrochloric was present very little sulphur dioxide will have been evolved on adding the thiosulphate.

Dilute the solution to 50-60 c.c. and boil to expel all or at least the greater part of the sulphur dioxide. This can be done by one or two minutes' brisk boiling if the precaution of having only small excesses of hydrochloric acid and thiosulphate has been regarded. Otherwise the expulsion takes much longer time, and not only involves a danger of losing a little arsenic by volatilization, but also causes sulphur to be precipitated, and this both obscures very small precipitates of arsenious sulphide in the subsequent operation and retards the filtration. The complete expulsion of sulphur-dioxide is not otherwise essential.

To the cold and clear solution add 7-10 c.c. strong hydrochloric acid and precipitate the arsenic with zinc sulphide as on page 104. Under favourable circumstances—*i.e.* when no free sulphur can separate—as little as 0.001 gram of arsenic trisulphide is distinctly observable. The precipitate is collected on a pulp filter, washed with five per cent. hydrochloric acid, traces of iron and any copper existing in the ore separated with sodium sulphide and the estimation of arsenic completed in the manner already described. Any antimony existing in the ore would probably be reckoned as arsenic.

#### **Alkalis.**

Dissolve three grams of the ore in hydrochloric and a few drops of nitric acid and filter. The insoluble residue may contain the greater portion of the alkalis. After ignition, therefore, decompose it with hydrofluoric acid, and only rather more sulphuric acid than is needed to leave all the non-volatile constituents as sulphates after the excess of hydrofluoric acid has been evaporated off. Boil the residue with water, or dilute hydrochloric acid if thought to be necessary, and add to the filtered ferric solution. Neutralize the bulk of the acid, add a small excess of barium chloride, and filter off the precipitated barium sulphate. Heat the filtrate thus obtained nearly to boiling, add an

excess of ammonium carbonate, make up to 305 c.c., and preserve 200 c.c. of the clear filtrate.

The preceding operations should have eliminated practically all the iron, aluminium, manganese, barium, calcium, magnesium, and phosphorus. In order to detect any remaining, evaporate the filtered 200 c.c. to dryness, heat gently, extract the residue with hot water, and filter off any insoluble portion.

The clear filtrate is acidified with hydrochloric acid, re-evaporated to dryness, ignited to low redness to drive off any ammonium salts, and weighed as a mixture of sodium and potassium chlorides. The weight of the combined or separate alkaline oxides is obtained as on page 217.

If the siliceous residue was very small or completely volatilized after ignition, then the main solution only need be dealt with.

### CHIEF CONSTITUENTS ON ONE SAMPLE.

When an abundant supply of ore is available the practice of estimating as many constituents as possible on the same sample is not a good one. But the care and exactness required to account for the full weight taken, as well as obtain accurate individual figures, makes it a good exercise for students; and occasions do sometimes arise in the analysis of both minerals and metals which require the work to be done on as small a sample as possible.

Dissolve one and a quarter grams of the ore in hydrochloric acid. If exigencies of material require it this should be done in a closed vessel, so that the amount of carbon dioxide may be determined; or otherwise, "Loss on Ignition" is determined before the sample is treated with acid. Add one or two c.c. nitric acid and evaporate the solution to dryness, but do not bake. 'Take up' in hydrochloric acid, collect the silica, and volatilize it with hydrofluoric acid. Return any alumina, etc., which had accompanied the silica to the main filtrate.

Neutralize the ferric solution and precipitate with a small amount of ammonium acetate. Collect the basic ferric acetate on a plain filter fitted to a ribbed funnel, and wash it three or four times with hot water containing a drop or two of the precipitant. Transfer as much of the precipitate as possible to the original beaker by means of a spatula, and dissolve the rest from the paper by dropping warm concentrated hydrochloric acid on to it, and washing with cold water.

Re-precipitate the dissolved ferric acetate with ammonia, collect on the previously used paper, wash, dry, ignite apart from the paper, and

weigh as  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5$ . Dissolve in hydrochloric acid, estimate and allow for the small amount of insoluble silica, reduce a fraction of the solution with sulphurous acid and titrate. The remaining fraction is used for a direct estimation of alumina by means of sodium phosphate and thiosulphate in case greater accuracy, or a confirmation of the indirect result deduced from the ferric oxide determination, is required.

The ammoniacal filtrate may be mixed with the acetate filtrate or thrown away according to the expected amounts of lime and magnesia. After evaporating to a suitable bulk the manganese is precipitated with bromine and a small excess of ammonia, avoiding contact of the solution and atmosphere as much as possible. Collect the manganic hydrate and ignite to mangano-manganic oxide, or estimate in any other convenient way.

The filtrate is then precipitated with ammonium oxalate, in order to estimate lime, and the subsequent filtrate used for the estimation of magnesia after driving out the large amounts of ammonium salts. By avoiding the use of fixed alkalis it is possible to estimate alkaline oxides in the magnesia filtrate.

The remaining constituents must be estimated on separate samples. Instructions in the form of tables for making analyses in similar ways to this have been published by Julien (*Chem. News*, xxiv. 292), and Morgan (*Jour. Soc. Chem. Ind.* 1894, 1023).

TYPICAL ANALYSES.

	Magne- tite.	R. Hema- tite.	B. Hema- tite.	Specular.	Black- band.	Clay- band.	Iron Sand.	Bog Ore.	Spathic Ore.
Ferric Oxide, .	28.00	86.60	89.46	87.11	—	—	59.57	67.50	—
Ferrous Oxide, .	63.60	—	—	—	47.31	47.31	23.14	—	50.00
Alumina, .	0.05	0.06	0.48	1.51	0.80	7.10	4.77	4.18	0.25
Manganous Oxide, .	0.01	trace	0.10	1.16	1.67	trace	—	1.45	2.10
Lime, .	traces	0.25	traces	1.00	1.79	0.97	—	0.47	2.70
Magnesia, .	1.00	trace	0.16	0.43	1.73	0.91	—	0.23	3.00
Silica, .	6.46	8.74	1.00	8.41	1.20	10.12	3.56	7.81	5.10
Sulphuric Acid, .	0.03	0.32	0.05	0.37	traces	traces	0.16	—	0.42
Phosphoric Acid, .	0.02	0.36	0.10	0.08	0.59	0.49	trace	0.18	0.10
Titanic Oxide, .	—	trace	—	—	—	—	8.80	—	—
Lead Protoxide, .	—	0.49	—	—	—	—	—	—	—
Copper Oxide, .	—	0.10	—	—	—	—	—	—	—
Water (hygros.), }	0.75	{ 1.94	8.90	—	1.80	0.56	—	17.81	—
Water (combined), }	—	{ 0.25	—	—	10.40	2.32	—	—	—
Carbonaceous, .	—	0.45	—	—	32.71	30.22	—	—	36.84
Carbon Dioxide, .	—	0.32	—	—	—	—	—	—	—
	99.92	99.88	100.25	100.07	100.00	100.00	100.00	99.63	100.51

The Analyses of “Blackband,” “Clayband,” and “Iron Sand” are by Wallace.

## MANGANESE ORES.

The black oxide of manganese, which was somewhat fetishly used by Sheffield steel makers for its cleansing and strengthening properties before the introduction of ferro-manganese alloys, and is still used as a flux, will serve as a typical ore. Mineralogically the black oxide may be pyrolusite, psilomelane, or a mixture of the two, and for a complete analysis there must be determined: manganese dioxide and monoxide, ferric oxide, alumina, baryta, lime, silica, sulphuric, phosphoric, and arsenic acids, and water and organic matter. For works' purpose trouble is rarely taken to determine more than the total manganese, crude silica, and relative freedom from sulphur and phosphorus.

### GENERAL ANALYSIS.

Digest one gram of the ore with 20 c.c. concentrated hydrochloric acid until only a siliceous residue is undissolved. Evaporate nearly to dryness, add 3 or 4 c.c. hydrochloric acid, dilute to about 150 c.c., add a drop or two of sulphuric acid, and allow the solution to stand overnight.

The residue is collected, washed with very dilute hydrochloric acid, and ignited. Besides silica it may contain barium sulphate, alumina, lime, etc.; fuse therefore with sodium carbonate, evaporate with hydrochloric acid, 'take up' with more hydrochloric and a drop or two of sulphuric acid, and after standing in a warm place for an hour or so, collect and weigh the mixture of silica and barium sulphate. The silica is volatilized with hydrofluoric and a drop of sulphuric acid, and its percentage calculated from the loss; the residue is barium sulphate, which must be calculated to oxide. The filtrate is precipitated with ammonia, and the residue (alumina) and the new filtrate (if it contains lime) added in their respective places in the analysis of the main portion.

Add five or six grams ammonium chloride and an excess of ammonia to the main filtrate to precipitate iron and alumina, but not manganese or lime. The small amount of manganese possibly carried down may be neglected unless it is being estimated on the same sample, and then it must be recovered by a re-precipitation. If a large amount of iron is present the ammonium chloride is omitted, and an acetate separation made as in an iron ore.



Dissolve the ferric and aluminic hydrates, together with the alumina recovered from the siliceous residue, in hydrochloric acid, and estimate the alumina by boiling with sodium phosphate and thiosulphate. Boil the filtrate with nitric acid, remove the liberated sulphur by filtration, precipitate the iron with ammonia (as phosphate), and estimate it volumetrically in the usual way. Any titanic oxide in the ore will be found partly with the silica and barium sulphate residue, but mostly with the precipitated aluminium phosphate, and on treating the latter with hydrochloric acid it will not dissolve to a clear solution as it should if pure.

The solution containing the manganese is diluted to at least half a litre, precipitated with bromine and *a small excess* of ammonia, boiled and filtered through a fluted paper. The manganic hydrate is washed with three per cent. nitric acid, the washings neutralized, the small amount of manganese they may contain re-precipitated and added to the bulk, and the whole ignited at the highest attainable muffle temperature before weighing as manganoso-manganic oxide. The lime is precipitated as oxalate from the combined filtrates after evaporating to about 150 c.c.

Estimated in the above manner the manganese would be somewhat too high and the lime too low, on account of the imperfect separation of the two whenever the former is precipitated as hydrated dioxide from neutral or alkaline solutions. A more accurate result is obtained by heating the solution to boiling, making strongly alkaline with ammonia, and passing a rapid stream of washed sulphuretted hydrogen gas until the manganese is completely precipitated; then filtering rapidly through a fluted paper and measuring the volume of filtrate and residue respectively, so as to avoid washing. The filtrate is evaporated, traces of manganese which have escaped precipitation as sulphide thrown out with bromine and ammonia, and the lime estimated as usual.

The remaining constituents are more conveniently determined on separate samples.

#### **Total Manganese.**

The volumetric determination is made as follows : Dissolve one gram in hydrochloric acid, add two or three c.c. hydrofluoric acid to break up silica compounds, and evaporate with 10 c.c. sulphuric acid to strong fumes : then dilute and filter.

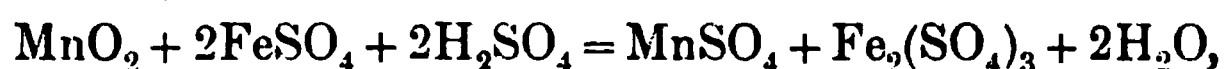
At this point hydrogen peroxide may be added to test for titanic oxide, which, if present, can be at once colorimetrically estimated.

Dilute the solution to 200 c.c., measure out 25 c.c., add 20 c.c. 1.42 nitric acid, and make the bismuthate estimation as in manganese alloys (page 127).

#### **Peroxide of Manganese.**

The respective amounts of manganese existing as dioxide and monoxide, although the information is of little value to the steel maker, must necessarily be determined in order to make a statement of a complete analysis.

From five to six decigrams of the iron 'flower' wire used for standardizing permanganate is dissolved in about 70 c.c. dilute sulphuric acid (1 to 3). When the last trace of iron has disappeared half a gram of ore ground as finely as possible in an agate mortar is weighed into a diminutive porcelain crucible, and slid bodily into the boiling acid ferrous solution. The flask is stoppered, except for a steam exit, and the solution kept boiling until the ore is completely decomposed, which, with very hard varieties, if properly ground, ought not to take more than fifteen minutes. The solution is then cooled, diluted, and titrated with permanganate or bichromate. The amount of peroxide can be calculated from the permanganate value of the ferrous sulphate actually oxidized. The equation is



whence  $1 \text{ c.c. } \frac{\text{N}}{10} \text{ KMnO}_4 = 0.00435 \text{ gram MnO}_2.$

Any ferrous oxide existing in the ore would introduce a negative error when the amount of peroxide was estimated in this way. If the ore is to be used for bleaching purposes, *i.e.* the production of chlorine, this error in the valuation is desirable, because it corresponds exactly with the available oxygen lost in practice. But from a strictly analytical point of view an absolute process would be preferable. There is a disposition to ignore the separate estimation of the small amounts of ferrous oxide as well as the afore-mentioned error it introduces, and from a steel-works' standpoint there is certainly no harm in doing so.

#### **Water and Organic Matter.**

These constituents are determined by heating two grams of the ore in a tube between plugs of recently ignited asbestos, and carrying the water and carbon dioxide formed, by means of a current of dried air, into a weighed potash bulb.

The combustion tube need not be more elaborate than a six or eight-inch piece of Jena-glass tubing (half-inch diameter) drawn out at one end to fit close up to the potash bulb with a rubber joint, and fastened to an

air-drying tube at the other by means of a perforated stopper made from thick-walled rubber tubing. The combustion tube is laid on a lamp screen, and, after starting the aspirator, heated with a bunsen burner.

### Sulphur.

To estimate the total sulphuric anhydride, digest two grams of the ore with hydrochloric acid, fuse the siliceous residue with sodium carbonate, extract the melt with water, and filter. The barium is left on the filter as carbonate; its associated sulphuric acid is in solution. Mix the two filtrates: if any silica is precipitated, then make freely acid, evaporate to dryness, and remove it; but if the solution remains clear, adjust the acidity with ammonia so that only a small excess of acid is present and add barium chloride. If any co-precipitation of the dissolved silica is feared, the ignited barium sulphate may be treated with hydrofluoric and a drop of sulphuric acid and re-weighed; but in our experience this has always turned out to be a needless operation.

The sulphuric acid in combination with barium may sometimes be estimated separately by boiling a suitable portion of the ore with hydrochloric acid, evaporating to low bulk, diluting, and allowing to stand a few hours. The collected residue is ignited, the silica driven off with hydrofluoric and sulphuric acids, the residue fused, dissolved in hydrochloric acid, and the solution, which contains all the barium, precipitated with an excess of sulphuric acid. The correctness of the result involves the assumption that no other compound of barium—*e.g.* the carbonate—is present, as well as no soluble sulphate which would cause barium sulphate to be formed during the hydrochloric acid treatment of the ore.

### Phosphorus.

Dissolve two grams in hydrochloric acid, filter off the siliceous residue and decompose it with hydrofluoric and sulphuric acids. If the ore contains titanite oxide, then separate the phosphorus from the manganous solution as basic aluminium phosphate, fuse the precipitate obtained along with the residue from the silica volatilization, and proceed further as with titanite irons on page 172.

But if no titanite oxide is present, then after volatilizing the silica and heating to strong fumes, add the sulphuric solution to that containing the manganese, collect the phosphorus as a basic ferric compound, redissolve the precipitate in nitric acid, and estimate the phosphorus *via* phospho-molybdate and lead molybdate in the usual way. Manganese ores generally contain arsenic.

TYPICAL ANALYSES.

Manganese Dioxide, -	89·00	85·12	66·03	69·00	29·47
Manganese Monoxide, -	3·26	0·68	10·39	1·34	3·46
Ferric Oxide, -	0·14	0·79	1·50	1·36	38·57
Alumina, -	0·64	1·80	1·60	2·76	3·32
Barium Oxide, -	0·33	1·58	3·58	2·20	0·64
Calcium Oxide, -	0·12	0·43	5·36	2·75	2·00
Magnesium Oxide, -	—	0·27	0·13	0·25	1·05
Silica, -	4·27	5·09	4·75	11·80	10·80
Sulphuric Acid, -	1·00	0·40	1·57	1·00	0·04
Phosphoric Acid, -	0·42	0·36	0·05	0·60	0·05
Titanic Oxide, -	0·25	—	—	0·10	—
Copper Oxide, -	—	—	0·14	—	—
Lead Oxide, -	—	0·18	0·05	—	—
Zinc Oxide, -	—	—	—	—	2·90
Carbon Dioxide, -	—	0·34	2·53	—	1·55
Arsenic, -	—	—	0·04	0·09	—
Alkalis, -	—	0·41	0·26	—	—
Water and Organic, -	0·47	1·95	1·96	6·60	6·20
	99·90	99·40	99·94	99·85	100·05
Analyst,	Authors.	Ernst.	Pattinson.	Authors.	Arnold.

TUNGSTEN ORES.

WOLFRAMITE.

This mineral is a tungstate of iron and manganese, which varies greatly in the percentage of ferrous and manganous oxides. In commercial samples the former ranges from ten to twenty per cent., and the latter from four to fourteen. The tungstic oxide usually lies between seventy and seventy-five per cent. An estimation of the main constituents is made as follows :

Fuse one gram of the agate-ground material with three or four times its weight of sodium carbonate. Extract the cooled melt with water, add a little sodium peroxide to destroy any manganates, and filter off the ferric and manganic oxides.

The clear filtrate is faintly acidified with nitric acid, and then made faintly alkaline with ammonia. If any alumina is precipitated on heating, it must be filtered off, dissolved in a little hydrochloric acid and evaporated so as to recover any co-precipitated tungstic oxide. If no precipitate is formed with ammonia, or after removing what may form,

then precipitate the tungsten with mercurous nitrate and mercuric oxide, and proceed further to estimate it as described under Method II. for the assay of ferro-tungsten alloys on page 146.

The ferric and manganic oxides are ignited to destroy the paper and then dissolved in a small quantity of hydrochloric acid, and the solution evaporated with 10 c.c. sulphuric acid until it fumes. Any tungstic oxide which had escaped separation by the fusion would be precipitated by this treatment, and, after diluting, and boiling the solution so as to re-dissolve the precipitated salts of iron and manganese, should be collected on a small filter and estimated.

The filtrate is made up to 200 c.c., 50 c.c. of it mixed with 20 c.c. 1.42 nitric acid and manganese estimated by the bismuthate process.

$$1 \text{ c.c. } \frac{N}{10} \text{ KMnO}_4 = 0.00142 \text{ gram MnO.}$$

Another portion of the filtrate is reduced with sulphurous acid and titrated with permanganate.

$$1 \text{ c.c. } \frac{N}{10} \text{ KMnO}_4 = 0.0072 \text{ gram FeO.}$$

If the small amounts of impurities in the mineral must be estimated, two grams are opened up by fusion as before, transferred to a porcelain dish as though it were a 'Refractory,' evaporated to dryness with hydrochloric acid, but not baked, and then boiled with dilute acid (1 to 5). The residue contains silica and tungstic oxide. The filtrate is analyzed as though it were an iron ore. We have had no experience of a reliable method for the estimation of the small amounts of tin and niobium (columbium) which are occasionally found in this mineral.

### SCHEELITE.

Samples of commercial scheelite can be opened out by fusion with alkalis or alkaline carbonates or by solution in mixtures of acids, of which hydrofluoric is one. In the latter case the silica cannot be determined, but the procedure does not cause any tungstic oxide to be volatilized as heating in the dry way with ammonium fluoride is said to.

The analysis is much simplified if care be taken at the outset to open out with hydrochloric acid alone. This can be done by heating one gram of the sample which has been finely crushed, but not necessarily agate-ground, with 60 to 70 c.c. concentrated hydrochloric

acid at a temperature quite below boiling point. The tungstate needs a little time to completely decompose. After stirring the undissolved portion is white, in a minute or two it becomes yellow. On repeatedly stirring, the coatings of tungstic oxide dissolve until finally nothing or only a siliceous residue remains. Any attempt to hurry the decomposition by boiling weakens the acid, causes a portion of the dissolved tungstic oxide to precipitate, and retards the operation as well as prevents its course being clearly observed.

Evaporate the solution barely to dryness, boil with dilute hydrochloric acid (1 to 5), filter, wash, and ignite in a tared platinum dish. The increased weight is due to silica and tungstic oxide.

The silica is estimated by volatilizing with hydrofluoric acid. The residue is pure tungsten trioxide, or contains not more than two or three milligrams of impurities. The small amounts of ferric oxide it may contain are allowed for after fusing with sodium carbonate, etc.

The filtrate is precipitated with ammonia, and the ferric hydrate dealt with as usual. The lime is precipitated as oxalate and weighed as oxide or sulphate. The following volumetric process for the estimation of lime gives excellent results :

Precipitate the calcium with oxalate as usual, and collect on a small asbestos filter. After thorough washing with faintly ammoniacal water, return the filter and its contents to the flask in which the precipitation was made, and digest with hot dilute sulphuric acid (1 to 6) until it is completely decomposed. The solution is then diluted with about its own bulk of water, heated to 70° C.—as high a temperature as the hand can well bear—and titrated with permanganate until a persistent pink tinge appears.

$$1 \text{ c.c. } \frac{N}{10} \text{ KMnO}_4 = 0.0028 \text{ gram CaO.}$$

The trade complaints sometimes made of the low results obtained when scheelite is opened out with acids and tungstic oxide recovered by evaporation, when compared with those obtained by alkaline fusion and precipitation as mercurous tungstate may be due :

1. To the evaporated residue being so strongly baked that some calcium tungstate is re-formed ; or to the common practice of using strong hydrochloric acid in re-dissolving the residue so that some tungstic oxide also is re-dissolved, and not again completely precipitated on diluting.

2. To the presence of molybdic oxide in the mineral. By the acid process this would not be estimated ; but by the fusion process it would

be precipitated along with the tungsten, and only partially driven off during the subsequent ignition.

Traube (who instances tin, fluorine, chlorine, cerium, didymium, lanthanum, magnesium, and copper as having been at various times observed in scheelite) examined ten samples of the mineral from different localities, and in every case found molybdic oxide varying from traces to 8.23 per cent.

The acid process is to be preferred always because it enables molybdenum to be easily looked for and estimated, and it also permits a complete analysis to be made in a simple manner.

TYPICAL ANALYSES.

	Wolframite.			Scheelite.		
Tungstic Oxide, -	74.86	71.68	76.00	79.90	70.97	77.54
Molybdic Oxide, -	—	—	—	—	1.00	2.03
Ferrous Oxide, -	13.45	19.68	11.03	—	—	—
Manganous Oxide, -	11.02	6.20	13.01	—	—	—
Stannic Oxide, -	—	0.65	—	—	—	—
Niobic Oxide, -	1.22	—	—	—	—	—
Lime, -	—	—	—	19.37	17.86	19.91
Silica, -	—	—	—	0.29	8.63	—
Ferric Oxide, -	—	—	traces	0.70	1.26	—
	100.55	98.21	100.04	100.26	99.72	99.48
Analyst,	Bodenbender.	Frenzel.	Authors.	Hoffmann.	Authors.	Traube.

CHROMIUM ORE.

CHROME IRON ORE: CHROMITE.

This material is used for the production of chromium alloys, for the manufacture of chrome bricks, and for the lining or beds of certain kinds of furnaces. The ore varies greatly in composition, which however generally falls within the following limits: Chromic oxide, 40 to 60 per cent; ferrous oxide, 16 to 35 per cent.; alumina, 2 to 20 per cent; magnesia, 5 to 18 per cent. Sometimes, however, magnesia is practically absent, but small amounts of silica and lime may nearly always be found. It is by no means safe to assume that samples taken from the same locality will have practically the same composition.

### Chromic Oxide.

This constituent is estimated as chromic acid after opening out the powdered ore either with the tribasic reagent or sodium peroxide. It is unnecessary, if the sodium peroxide fusion is well made, to have the ore finer than passes through a sixty-mesh sieve.

$$1 \text{ c.c. } \frac{N}{10} \text{ K}_2\text{Cr}_2\text{O}_7 = 0.00254 \text{ gram Cr}_2\text{O}_3.$$

### Manganese, Sulphur, Phosphorus.

These constituents are also estimated as in ferro-chromium.

### Water, Organic Matter, etc.

The volatile constituents are estimated as in iron or manganese ores.

### Silica.

The silica can be estimated as is silicon in ferro-chromium alloys (page 130), or otherwise as follows :

Mix one gram of the ore with four grams of sodium peroxide in a nickel crucible and fuse. Keep the crucible at scarcely visible redness, and the fused mass in constant motion for about two minutes. Dissolve the cooled melt in water, transfer to a porcelain dish, and add an excess of hydrochloric acid : everything should pass into solution. Evaporate to dryness, but do not bake strongly, take up again in hydrochloric acid and filter off the (probably) impure silica. Ignite, treat with hydrofluoric acid, and calculate the percentage silica from the loss.

### Iron, Alumina, Magnesia, Lime, Chromium.

These constituents may be conveniently estimated on one sample in the following manner : Open out one gram of the ore with sodium peroxide. Dissolve the melt in water, boil a few minutes to destroy any undecomposed sodium peroxide, and allow the insoluble oxides of iron, magnesium, calcium, nickel, and (if present) manganese to settle. The solution contains the chromium, aluminium, practically all the silica, and possibly also traces of lime and magnesia. Pour the clear liquid through a pulp filter and wash the residue by decantation, using 60 to 80 c.c. of water at a time until the washings are perfectly colourless.

Digest the filter with hydrochloric acid so as to dissolve the oxides which have passed on to it. Strain off the paper with a small filter plate, allow the acid solution to run into the beaker containing the bulk



of the oxides, and add as much acid more as will dissolve everything to a clear solution and leave a good excess.

The iron is then precipitated with ammonia and re-precipitated, and the ferric hydrate finally dissolved in hydrochloric or sulphuric acid, reduced to the ferrous state, and titrated.

$$1 \text{ c.c. } \frac{N}{10} \text{ KMnO}_4 \text{ or } \text{K}_2\text{Cr}_2\text{O}_7 = 0.0072 \text{ gram FeO.}$$

Although the total iron is generally calculated to ferrous a portion possibly exists as ferric oxide.

The combined filtrates are made, not faintly as usual, but decidedly ammoniacal, and the lime precipitated as usual. If the collected calcium oxalate is green it must be re-dissolved in strong hydrochloric acid and re-precipitated. It is also necessary to bear in mind the precautions given on page 220 if much magnesia is present.

If it is thought desirable to concentrate the filtrate from the calcium oxalate it must be kept ammoniacal during the evaporation, otherwise a compound of nickel is precipitated and much bumping ensues. The magnesia is finally precipitated with microcosmic salt in the usual way. The ignited pyro-phosphate should contain little or no trace of nickel.

Alumina may be separated from the alkaline chromic liquor in a variety of ways. One of the least troublesome, if circumstances permit, is to arrange a gas generator so that a steady stream of carbon dioxide may pass through the solution all night. On the following morning the precipitated basic carbonate is collected, washed, and ignited to alumina. In very exact analysis the basic carbonate may be dissolved in hydrochloric acid and re-precipitated with ammonia so as to eliminate any lime or magnesia which have originally passed into solution; but generally this extra operation is not worth the trouble.

But if only a small amount of alumina is present, or if the analysis must be completed without delay, then, after adding a faint excess of hydrochloric acid, add sodium phosphate, and as much ammonium acetate as is needed to destroy the free hydrochloric acid. Filter off the precipitated aluminium phosphate, wash until free from chromic acid, ignite, and weigh. Alumina cannot be completely separated from chromic acid by adding small excesses of ammonia or ammonium carbonate.

The filtrate is acidified, halved, and chromium estimated as before with ferrous sulphate and bichromate.

TYPICAL ANALYSES.

Chromio Oxide, - -	55·47	42·20	59·46
Ferrous Oxide, - -	16·20	15·68	19·21
Alumina, - - -	6·02	14·86	16·00
Magnesia, - - -	16·59	15·10	1·57
Lime, - - - -	0·67	0·86	0·52
Silica, - - - -	3·10	7·03	2·01
Sulphuric Acid, - -	0·10	0·13	0·05
Phosphoric Acid, - -	0·05	0·07	0·07
Water and Organic, -	1·60	3·03	0·97
	99·80	98·96	99·86

## PART VI. ANALYSIS OF REFRACTORY MATERIALS.

### ACID MATERIALS.

**Ganister, Silica Brick, Sand, Fireclay, Moulding Composition, etc.**

To determine the minor constituents of ganister, silica bricks, and sands with accuracy it is necessary to examine the reagents used as flux. A large amount of sodium carbonate, which is the most important reagent, should be well mixed and preserved in a stoppered bottle inscribed with the amount of each impurity per ten grams. The labour of estimating its silica, alumina, ferric oxide, sulphuric acid, etc., need not often be undertaken if the material is used only when these impurities are worth consideration.

### GENERAL ANALYSIS: AFTER FUSION.

Shake one gram of the powdered sample with three or four grams of sodium carbonate in a stoppered weighing bottle, transfer to a platinum dish and fuse. If the fusion is made in the muffle the platinum is not appreciably attacked as it is by fusing over a blast lamp, when some parts of the dish are made much hotter than and some not so hot as is necessary to fuse the mixture.

**Silica.**—Dissolve the melt from the platinum and transfer to a porcelain dish. Add an excess of hydrochloric acid through a hole in the cover so as to avoid loss by effervescence, and evaporate the clear or almost clear solution to dryness. The evaporation can be conveniently made in a flat-bottomed dish, without fear of spirting, and in a comparatively short time, by means of the arrangement used for ferro-tungstens on page 148.

No amount of baking of the dried mass appears to render all the silica quite insoluble; in fact, where considerable amounts of alkaline

earths are present, strong baking may defeat its own ends by forming silicates, which are soluble in the acid subsequently used. Two evaporations therefore are necessary when an accurate result is of great moment. In the first the dried mass should be heated to drive off all free acid, but not to decompose the ferric chloride. Then after taking up in hydrochloric acid and collecting the silica, the filtrate is re-evaporated in the same way. The small amount of silica—generally about one per cent.—which remains to be collected is ignited along with the bulk.

The ignition should be made at as high a temperature as possible to drive off the water completely and make the silica non-hygroscopic. The time and trouble needed to do this thoroughly cause it to be often left undone. It is necessary then to make two weighings. The first will be too high, on account of the water absorbed during the operation, but it enables the rider to be fixed at what is probably the correct weight. The second weighing is then made, after cooling in an air-tight and otherwise good desiccator, by transferring quickly to the balance pan, releasing the beam, and making any needed correction in the former weight from the swing of the pointer on the indicator.

A weighing made in the usual manner may be as much as a centigram too high. Ninety-five centigrams of silica left all night in a closed balance case gained eight per cent. A large number of works' analyses, although not scientifically precise, are very near the truth on account of this latter error and that due to incomplete insolubility of the silica after one evaporation balancing each other.

The silica is evaporated with hydrofluoric acid, the percentage calculated from the loss, and any residue added to the filtrate.

**Alumina and Ferric Oxide.**—Add a small excess of ammonia to the filtrate, boil, and filter off the precipitated ferric and aluminic hydrates. If these constituents are to be expressed together, the washed precipitate needs merely drying, igniting, and weighing; but if they are to be expressed separately, the iron in the weighed precipitate is determined volumetrically, its ferric oxide equivalent deducted from the total weight, and the alumina obtained by difference. This is a very well-known way, and has simplicity if not always the greatest possible accuracy to recommend it.

When large precipitates of the mixed hydrates have to be dealt with, it is better to proceed as follows: Dissolve in dilute hydrochloric or sulphuric acid, and precipitate the alumina as phosphate from the whole or a fraction of the solution by boiling with thiosulphate as on page 174. If only a portion of the solution has been used, the

remainder is reduced with sulphurous acid and the iron determined with permanganate or bichromate. But if, the amount of iron and alumina being small, all the solution was boiled with thiosulphate, then the filtrate must be boiled with nitric acid, the liberated sulphur filtered off, the iron precipitated with ammonia, collected, and estimated volumetrically.

**Lime and Magnesia.**—When lime and magnesia are present only in small amounts and their separation from iron and alumina is made in the presence of considerable ammonium chloride, without undue delay in the filtration, it is generally unnecessary to repeat the precipitation in order to recover doubtful traces of the former oxides. It may be advisable when either pair of elements is present in large amounts, and it certainly is when large amounts of both pairs are being handled.

Evaporate the solution to about 150 c.c. and precipitate the lime by adding a small excess of ammonia and a large excess of ammonium oxalate. Boil the solution a few minutes so as to promote the formation of a crystalline precipitate, allow it to cool, collect the calcium oxalate on a pulp filter, and wash with water containing a few drops of ammonia and ammonium oxalate. This wash mixture dissolves less of the precipitate than does water, and defeats any tendency the precipitate may have to pass the filter.

The washed oxalate is ignited as strongly as possible and weighed as oxide. But in order to obtain a less hygroscopic form, and in some degree to check the purity of the lime, it is customary to add a few drops of sulphuric acid, drive off the excess at the mouth of the muffle, and weigh as sulphate ( $\text{CaSO}_4 \times 0.412 = \text{CaO}$ ). The percentage calculated from the quickly weighed oxide should agree very well with that calculated from the sulphate.

The filtrate from the lime is evaporated as much as possible without its contained salts crystallizing out, about one-third its volume of strong ammonia added, and then an excess of a saturated sodium hydrogen phosphate solution. After standing for at least several hours with occasional stirring, the ammonium magnesium phosphate is collected, ignited, and weighed. For particulars of ignition, see Estimation of Magnesia in basic bricks, page 221.

### ALTERNATIVE PROCESS TO FUSION.

The difficulties of making a direct determination of silica and the contamination with sodium salts of precipitates, which at best are not

easily washed, has led to the following indirect determination of silica and a less objectionable determination of the other constituents. The process is suited for the analysis of ganister, silica bricks, and other forms of impure silica rather than for clay.

One or two grams of the finely ground material are treated in a tared platinum crucible with hydrofluoric acid, and at least as much sulphuric acid as will combine with the alumina and titanic oxide present. Allow the solution to stand over-night in a warm place, then evaporate to dryness, ignite, and weigh. The residue is treated with hydrofluoric, a drop of sulphuric, and a little hydrochloric acid, slowly evaporated, and again ignited and weighed so as to be certain that practically all the silica is eliminated.

A muffle is not generally hot enough to completely drive sulphuric acid out of combination with alumina and titanic oxide, so that the amount of silica is not accurately measured by the loss in weight, unless an excess of ammonium carbonate is added to the nearly dried residue, and the crucible strongly ignited to constant weight over a powerful blast lamp. The residue, which consists of ferric oxide, alumina, lime, and magnesia, is dissolved (by means of fusion if necessary) in hydrochloric acid, and the solution analyzed as before.

#### **Titanic Oxide.**

The presence of titanic oxide in fireclays has been investigated by Riley (*Quart. Journ. Chem. Soc.* 1862, xv. 311), who claims to have detected it in every clay examined. The highest and lowest results quantitatively determined were 1.05 and 0.42 per cent. Some very old analyses show the presence of titanic oxide in crucibles in amounts varying from 3.5 per cent. upwards, but it is very doubtful whether they are trustworthy. The authors have observed as much as one per cent. titanic oxide in the Derby (Edensor) fireclay so much used in Sheffield for crucible making, and a like amount in a silica brick of German manufacture.

In general analyses, made according to the above scheme, titanic oxide has been found partly with the silica, but mostly with the alumina. It may be colorimetrically determined by opening out a sample with hydrofluoric and sulphuric acids, evaporating until the former acid is eliminated, diluting the strong sulphuric solution, and making the hydrogen peroxide test as on page 95. Its amount in the weighed alumina or aluminium phosphate precipitate is determined by fusing with sodium carbonate, dissolving in sulphuric acid, and adding hydrogen peroxide, etc.; it is then allowed for by subtracting the

actual amount found in the former case and its  $\text{TiO}_2 \cdot \text{P}_2\text{O}_5$  equivalent in the latter.

### Ferrous Oxide.

The ferrous iron in refractory materials as well as in the siliceous residues of iron ores is always determined by some modification of one of the following processes :

(a) Fusion with mixed alkaline carbonates or acid potassium sulphate.

(b) Digestion with acid in sealed tubes at elevated temperatures.

(c) Treatment with hydrofluoric and a stronger acid, or with a mineral acid and some normal fluoride.

In each case the operation must be performed, in an atmosphere of carbon dioxide or purified coal gas, on very finely powdered material. The last process is most used and is said to give the most accurate results, although obviously the presence of organic matter, or pyrites, or metallic particles will spoil the determination whichever process is used.

The following is essentially Willbur and Whittlesey's mode of carrying out the process originally suggested by Avery : Mix the powdered sample intimately with from one to one and a half times its weight of fluorspar or cryolite (free from iron) in a platinum crucible, cover with hydrochloric acid, and heat in an atmosphere of carbon dioxide or sulphuretted-hydrogen-free coal-gas, until the materials are all dissolved. The time required for this will vary with the degree of fineness and the nature of the material, but the operation needs very little attention if carried out in some such arrangement as is shown in Fig. 14. This apparatus consists of a bottomless bottle standing in a shallow leaden dish, which is kept supplied with water so as to make an air-tight joint. The tube *A* is for the entrance of the neutral atmosphere and *B* for its exit. When decomposition is complete the cooled solution is diluted and titrated with bichromate.

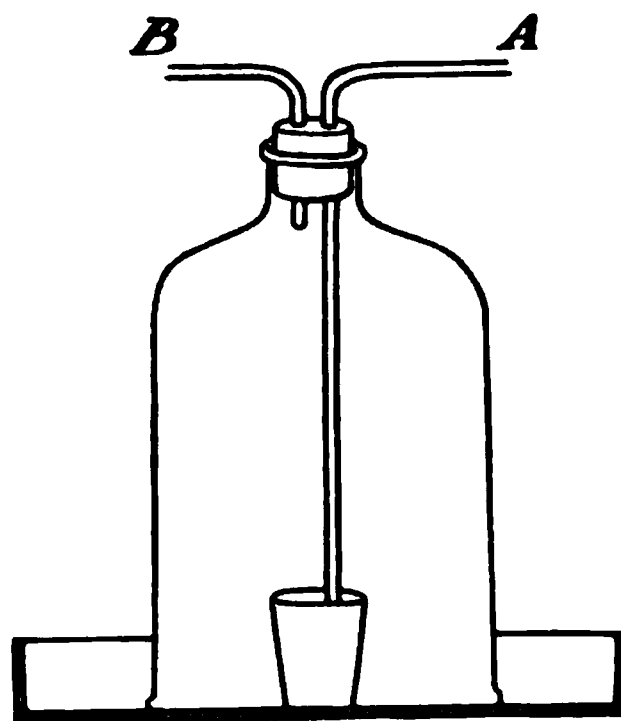


FIG. 14.

Hydrofluoric and sulphuric acids may be used instead of hydrochloric acid and fluorspar, but if much calcium is present the complete attack is retarded by the formation of calcium sulphate. Commercial hydro-

fluoric acid frequently contains small amounts of sulphur dioxide and other reducing agents. The error these would introduce must be avoided by adding just enough permanganate to oxidize them.

### Alkalis.

Only two methods designed especially for the estimation of alkalis in insoluble siliceous bodies are practised to any considerable extent: they are the 'Hydrofluoric acid' and the 'Lawrence Smith' processes.<sup>1</sup> There are, however, means of opening out silicates for general analysis, which permit also of alkali determinations being made: *e.g.* fusion with the oxides or basic salts of lead or bismuth.

#### *Lawrence Smith Process.*

The reagents used must be free from fixed alkalis. Carbonate of lime is prepared by dissolving the purest obtainable marble in hydrochloric acid, adding a little slaked lime to precipitate any ferric oxide, alumina, and phosphoric acid, and then precipitating the hot diluted filtrate with ammonium carbonate. The ammonium chloride it is proposed to use should leave no residue on ignition.

One gram of the sample, after grinding very thoroughly in an agate mortar, is mixed with its own weight of ammonium chloride and six or eight times its weight of calcium carbonate. The caustic lime formed on heating the mixture decomposes the silicate and converts the alkalis to chlorides. The crucible should be kept for about an hour at a bright red heat; there is no advantage in heating more strongly, as it causes the mass to vitrify or might even volatilize a little sodium chloride.

The strongly-sintered mass is loosened from the crucible by digesting with water and then transferred to a porcelain dish, and still further digested with more water. There is some danger of this and the subsequent operation taking up alkali from glass vessels if they were used—particularly new ones. The precipitate, which consists of the excess of lime and lime compounds of the silicates' components, is filtered off and washed.

The filtrate is treated with an excess—two or three grams—of ammonium carbonate, and after warming to granulate the precipitate somewhat again filtered and washed. The filtrate is evaporated to low bulk and again tested with ammonia and ammonium carbonate to make sure that all the lime has been removed. The solution is now free

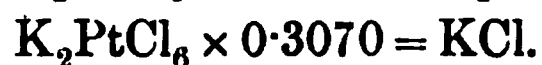
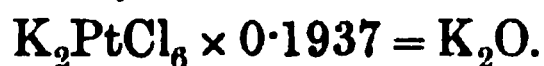
<sup>1</sup> An earlier process, which depends on the fusion of the powdered silicate at white heat with the carbonate or nitrate of barium, is described in Normandy's edition of Rose's *Quantitative Analysis*, p. 467.



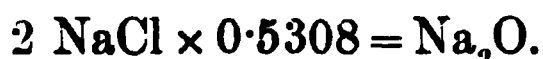
from all bodies except the fixed alkalis and volatile ammonium salts. The latter may be driven off by gentle ignition over a bunsen burner, but a much more elegant way, and one less likely to occasion loss through spirting, is to add about 3 c.c. nitric acid for each gram of ammonium chloride judged to be present, and boil gently to dryness in a tared dish. The residue is moistened with hydrochloric acid, re-evaporated, ignited gently, and weighed as chlorides.

The total weight of the alkaline oxides is obtained by dissolving the chlorides in water, estimating the chlorine (by titrating with standard silver nitrate and potassium chromate, or otherwise) and substituting oxygen for chlorine in atomic proportions. That is to say, deduct the total weight of chlorine found from the weight of the mixed chlorides, and then add the former weight multiplied by 0.2254 to the remainder.

To estimate the oxides of sodium and potassium separately add an excess of platinic chloride to the dissolved alkaline chlorides, evaporate to as low a bulk as possible without actual crystallization and dilute with an equal volume of alcohol. Filter on to a tared paper, or preferably through a Gooch crucible, dry at 120° C. and weigh.



The sodium chloride is determined by difference and the oxide calculated from it.



#### *Hydrofluoric Acid Process.*

Moisten one or two grams of the finely powdered material with sulphuric acid, add 30-40 c.c. hydrofluoric acid, and heat gently until every trace of grit has disappeared, then evaporate to dryness and ignite. Dissolve the residue as far as possible by digesting with hydrochloric acid, dilute the solution to about 200 c.c. with water, add a small excess of ammonia, boil, and filter. If the precipitate is a bulky one, a fraction only of the solution need be used.

Add a little barium chloride, and then successively ammonium carbonate and phosphate, and filter off the separate precipitates of barium and calcium carbonates and magnesium phosphate. This final filtrate, which contains only fixed alkalis and ammonium salts, is then dealt with as in the Lawrence Smith process.

#### **Water and Organic Matter.**

These constituents, and any small amount of carbon dioxide are generally expressed as 'Loss on Ignition' with sufficient exactness for

works' purposes. But when the item is a large one—*e.g.* in fireclays—its components may be shown separately.

*Hygroscopic Water* is determined by heating from ten to twenty grams of the clay in a shallow tared platinum dish at 100° C. for two or three hours, and then further until a weighing made after an additional hour's heating does not differ materially from the previous one. Any required crushing or grinding of the clay should be done prior to this determination if the further analysis is being made on the dried portion, because it readily absorbs water from the atmosphere.

*Combined Water and Organic Matter* are determined by heating two grams of the material in a dried tube of refractory glass as in manganese ores (page 202). The tube should contain an inch or so of copper oxide and a plug of asbestos to prevent the escape from the tube of carbon monoxide and any fine dust. The combustion is continued until the water deposited in the cooler part of the tube is swept completely into the weighed tube containing calcium chloride or sulphuric acid. By that time all organic matter will have passed as carbon dioxide into the weighed potash bulb arranged next in the train. From the increased weight of the separate absorbers the percentages of combined (or plastic) water and organic matter are calculated.

The combined water and organic matter are frequently obtained and shown together by merely igniting one or two grams of the dried clay. The result thus obtained diverges from the truth according as small or large amounts of ferrous oxide are present.

### MOULDING COMPOSITIONS.

These are mixtures of ground siliceous and clayey materials, such as old fire-bricks and steel-making crucibles, with more or less plumbago, charcoal, or other form of carbon. Various impure forms of glucose and brewing residues are also added for special purposes. The value of these compositions depends largely on the physical characters of the material, and a chemical analysis should therefore be accompanied at least by such a mechanical analysis as can be made by shaking a few grams of the material in a test tube and carefully examining the stratified layers.<sup>1</sup>

After driving off moisture and carbonaceous matter by ignition, the mineral residue is examined by the methods already given. An

<sup>1</sup> A suggestive section on the Mechanical Analysis of Clays is given in Fresenius' *Quantitative Analysis*, vol. ii., page 265, 7th edition.

analysis of a steel-melting pot, so much sought after for making these compositions, is given on page 222.

## NEUTRAL MATERIALS.

## Bauxite, Chrome Bricks, Plumbago.

*Bauxite* is well known to the analyst on account of the titanic oxide it almost invariably contains. Titanic oxide has been called "the steel chemist's horror"; the dread, however, is a purely superstitious one.

Hygroscopic and combined water are determined as in fireclays. The sample is then opened out by fusion with sodium carbonate. The silica is obtained by evaporating with acid ; it always contains a little titanitic oxide, which is left wholly in the residue after the former is volatilized with hydrofluoric acid. The iron is determined volumetrically in a portion of the filtrate and the alumina—as phosphate—in another portion. This aluminium phosphate contains all the titanitic oxide, except that found with the silica.

According to Deville, who examined samples from various localities, bauxite may contain alumina in both the crystallized (corundum) and amorphous state, and also more or less carbonate of lime and phosphoric and vanadic acids.

*Chrome Bricks* are analyzed by the processes given for chromite on page 207.

*Black Lead* for foundry use, or plumbago pots are very rarely submitted to any chemical examination beyond determining 'Loss on Ignition.' An actual determination of the carbon is nearly always less than the figure thus obtained, on account of the presence of water or some other volatile constituent. The ash may be examined by processes already described. The following is an analysis of black lead used for steel-foundry purposes:

Loss on ignition,	-	-	-	-	-	-	-	59·24
Silica,	-	-	-	-	-	-	-	21·40
Ferric oxide,	-	-	-	-	-	-	-	8·05
Alumina,	-	-	-	-	-	-	-	9·56
Manganous oxide,	-	-	-	-	-	-	-	0·28
Lime,	-	-	-	-	-	-	-	0·70
Magnesia,	-	-	-	-	-	-	-	0·56
								99·79

## **BASIC MATERIALS.**

### **Lime or Magnesia Bricks, Dolomite, Limestone, etc.**

With this class of material the possibility of error is perhaps greatest in those cases where a little lime has to be separated from much magnesia. The analysis of a magnesite brick will therefore be described, and the obvious modifications required to fit the processes to the analysis of dolomite, etc., left to the operator's discretion.

### **Silica.**

Weigh one gram of the powdered brick into a small beaker, moisten with water, add 20 c.c. hydrochloric acid, and boil vigorously until a colourless residue of impure silica only is left. Evaporate to dryness, take up with hydrochloric acid, and filter. The ignited silica is volatilized with hydrofluoric acid and any small residue dissolved and added to the main filtrate.

### **Alumina and Ferric Oxide.**

In order that no appreciable amount of either lime or magnesia may be precipitated with the iron and alumina on adding ammonia, it is necessary to add a few grams of ammonium chloride, or to have so considerable an amount of free hydrochloric acid as will produce it when neutralized. Even with this precaution the earthy oxides will certainly be precipitated if the solution is kept boiling for some time. As soon therefore as the hot solution, to which the small excess of ammonia was added, begins to boil, remove it from the burner and filter as quickly and as much out of contact with the air as possible. When these particulars are attended to there seems to be no need to dissolve and re-precipitate the small amounts of ferric and aluminic hydrates, and they may therefore be at once estimated in the manner indicated on page 212.

### **Lime.**

Dilute the filtrate to 700 or 800 c.c., add eight or ten grams more ammonium chloride, and then as much ammonium oxalate as is equivalent to both the lime and magnesia. The hot solution—which must not be boiled—is allowed to cool thoroughly with occasional stirrings, and then filtered. The large dilution recommended is necessary in order to keep up the bulk of magnesia, though it could prob-

ably be lessened somewhat if the lime were precipitated from the cold solution. The large excess of ammonium oxalate is necessary to counteract the solvent action of magnesium chloride on calcium oxalate: ammonium chloride exerts no appreciable solvent action.

Notwithstanding these precautions some magnesia is invariably precipitated<sup>1</sup> along with the lime. After filtering the cold solution, the precipitate is re-dissolved in hydrochloric acid, and re-precipitated from a faintly ammoniacal solution in the same way as before, except that less dilution and less ammonium chloride are needed to completely prevent the precipitation of the remaining magnesia. The second precipitate is filtered off in due course and estimated either as oxide or sulphate in the usual manner.

#### **Magnesia.**

The combined filtrates are acidified and evaporated to 500 c.c., or some other convenient volume. From 100 to 200 c.c. of this solution is measured into a flask along with one-third its volume of strong ammonia, and an excess of a saturated solution of sodium ammonium phosphate is added in drops from a burette to the vigorously shaken liquid. A very tolerable result is obtainable by filtering off the precipitated ammonium magnesium phosphate after shaking the closed flask for about five minutes, but it is customary to allow at least several hours for the magnesia to settle out.

Collect the precipitated phosphate on a pulp filter and clean out the flask with separate portions of the clear filtrate. Then wash with strongly ammoniacal water, using a little at a time by preference, until the washings give a scarcely perceptible opalescence when an excess of nitric acid and silver nitrate are added.

The somewhat bulky precipitate is dried at the mouth of the muffle and the paper ignited from it at as low a temperature as possible. When the precipitate is nearly white, and not before, the dish may be pushed well into the muffle, strongly ignited, and then weighed. Any lumps in the perfectly white precipitate should be broken in order to make sure that they contain no undecarbonized paper, as they are apt to when the ignition is pushed too quickly. It is as well also to dissolve the precipitate in hydrochloric acid, and note that small black particles or other insoluble matter is absent.

For modes of assisting the complete combustion of organic matter in the presence of phosphates see the phosphorus bibliography.

<sup>1</sup> Ammoniacal solutions of magnesium oxalate containing no lime whatever deposit precipitates in the course of a few days' standing.

Manganese.

The estimation of manganous oxide in Dolomite or Lime-stone is a very simple affair. The Red-Lead process described on page 32 appears to have been used for this purpose some time before it came into use for the assay of steel.

Phosphoric Acid.

Five to ten grams of the material are digested with hydrochloric acid and filtered. The ignited siliceous residue is treated with hydrofluoric acid, and any remaining portion dissolved and added to the bulk of solution. There should be enough ferric oxide or alumina present to more than combine with the phosphoric acid, but if not add a little ferric chloride or nitrate and a small excess of ammonia. Dissolve the precipitated basic ferric, or aluminic phosphate in nitric acid, and make the molybdate separation and the lead molybdate estimation of the phosphorus as usual.

This class of material may also contain small amounts of occluded minerals, for the determination of which no specific instructions can be given. Pyrites, rutile, and fluorspar occur most commonly. The two forms of water and alkalis may of course be present : they are estimated as in fireclay.

TYPICAL ANALYSES.

	Silica Bricks.		Fireclay.	Magnesia Bricks.		Ganister.	Old Crucible.	Bauxite.
Silica, - - -	96.47	95.00	45.00	6.45	7.26	98.76	48.97	9.87
Alumina, - - -	1.25	1.21	34.32	1.50	1.74	0.67	40.08	34.57
Ferric Oxide, - - -	1.05	0.76	1.92	1.13	1.35	0.37	—	27.93
Ferrous Oxide, - - -	—	—	—	—	—	—	3.40	5.08
Lime, - - -	1.30	2.01	0.80	2.01	5.62	0.06	0.56	0.91
Magnesia, - - -	traces	—	0.50	89.18	84.00	0.09	0.73	0.62
Titanic Oxide, - - -	—	0.96	1.06	—	—	—	0.70	3.51
Carbon, - - -	—	—	—	—	—	—	3.07	—
Iron, - - -	—	—	—	—	—	—	2.43	—
Water (hygros), - - -	—	—	3.60	—	—	—	—	} 19.36
Water (combined), - - -	—	—	12.30	—	—	—	—	
Alkalis, - - -	—	—	0.70	—	—	—	0.50	—
	100.07	99.94	100.20	100.27	99.97	99.95	100.44	101.85

The analysis of Bauxite is by Riley.

## PART VII. ANALYSIS OF SLAGS.

WHEN slag is run into thin and quickly-cooled pieces, it is practically homogeneous ; there is therefore no difficulty in taking a fair sample. The quick cooling has often also the effect of converting an otherwise insoluble into a soluble slag. Very large masses of slag which cool slowly are not usually homogeneous ; indeed, the interior of such masses may be porous, and may, particularly with basic material, be lined with perfect crystals of the slag's constituents. See Stead and Ridsdale (*Journ. Iron and Steel Inst.* 1887, i. 222).

The instructions already given in the parts dealing with ores and refractory materials would enable any of the customary slags to be analyzed ; it is desirable, therefore, to give no more than outline descriptions and a few analytical requirements of a special kind. This may be conveniently done by considering separately : Blast, Acid Siemens, Basic Siemens, and Puddling Furnace Slags.

### BLAST FURNACE SLAG.

An experienced eye may deduce something of the chemical composition of a slag by carefully observing its physical characters during the working of a furnace. The colour differences are the most obvious : violet, yellow, black, and blue slags being said to correspond respectively with the presence of notable amounts of manganous oxide, manganous sulphide, ferrous oxide, and the oxides of aluminium and zinc, or the sulphide of sodium. A broader distinction which there are more opportunities of verifying is that furnaces making grey iron yield a light-coloured, and those making white iron a dark-coloured slag ; the ferrous oxide in the former case being under one per cent., and in the latter (often considerably) over one per cent.

**Silica.**—Weigh one and a quarter grams of the ground slag, which should have been magnetically freed from metallic shots, into a small

wide beaker, add 10 c.c. water, and boil. Then add 15 c.c. hydrochloric acid at such a rate that the boiling is not disturbed. This mode of dissolving siliceous bodies prevents the undissolved portions being coated over with gelatinous silica. Boil briskly until the solution is nearly dry, add a few drops of nitric acid, and continue to heat until all smell of hydrochloric acid has gone. The silica separates at the surface and leaves the liquid clear to the last.

Take up the evaporated residue with hydrochloric acid, filter off the silica, ignite, and weigh. The residue may not be quite pure silica, but as a single evaporation does not make the whole of it insoluble the error is balanced to some extent, and the results are considered accurate enough for works' purposes. When a slag contains notable amounts of barium sulphate or titanous oxide, it may be necessary to make a further examination of the ignited silica.

If aluminous ores are being smelted and fluxed with magnesian limestone, it is never safe to omit treatment of the silica with hydrofluoric acid, because spinel (magnesium aluminate) to the extent of two or three per cent. may be present (Shimer). If a further examination of the spinel is needed it must be fused with bisulphate or caustic alkalis because it is not appreciably attacked by acids or fusion with sodium carbonate.

**Iron and Alumina.**—Dilute the filtrate to about 200 c.c., add two or three grams of ammonium chloride unless a large excess of hydrochloric acid is present, and precipitate ferric and aluminic hydrates with ammonia. Cool, make the solution up to 250, and filter off 200 c.c. The precipitate may be washed, ignited, and weighed as alumina and ferric oxide, but a thorough washing takes as much time as is required to return the drained precipitate to the beaker, warm with dilute hydrochloric acid, strain off the paper through a filter plate, wash, add about three grams of sodium phosphate, and precipitate aluminium phosphate as in the assay of ferro-aluminium alloys.

The filtrate is then oxidized with nitric acid, and the iron determined as on page 212; or a separate two grams dissolved as in the first instance, diluted, reduced, and titrated with bichromate. Blast furnace slags containing very little iron and considerable calcium sulphide need no reduction, as the iron, after dissolving, exists entirely as ferrous oxide.

**Lime and Magnesia.**—If much manganese is present, the solution (200 c.c.), filtered from the aluminic and ferric hydrates, is treated with bromine and a small excess of ammonia, and the manganic hydrate filtered off and washed. The lime is then precipitated as oxalate, and



ignited to oxide<sup>1</sup> or sulphate, or estimated volumetrically as on page 206. Magnesia is precipitated from the filtrate and weighed as pyrophosphate as usual.

**Manganese.**—Boil one gram of the powdered slag with 20 c.c. water, and add 10 c.c. 1.42 nitric acid. When the slag is decomposed, or nearly so, add a few c.c. hydrofluoric acid to decompose any undissolved portion and destroy the dissolved silica which might otherwise impede the subsequent filtration. Treat the cooled solution with bismuthate and estimate the manganese as in steels.

$$1 \text{ c.c. } \frac{N}{10} \text{ KMnO}_4 = 0.00142 \text{ gram MnO.}$$

The red lead process may also be used if not much manganese is present.

**Sulphur.**—Sulphur may be estimated gravimetrically by the nitrohydrochloric acid process used for steels (page 43); but more simply by regarding the crushed material as a coke which has been roasted with the tribasic reagent (see page 233). From this point of view it is only necessary to weigh one gram of the finely powdered slag into a small flask, add 10 c.c. water, about 2 c.c. bromine, and 10 c.c. hydrochloric acid. On gentle warming the slag is dissolved and the sulphur completely oxidized to sulphuric acid. Dilute then with an equal volume of water, boil off the excess of bromine, pass through a small filter, add ammonia to the filtrate until the precipitated aluminic hydrate redissolves somewhat lazily, and then an excess of barium chloride. The precipitated barium sulphate is prepared for weighing as usual.

As the sulphur exists almost entirely as calcium sulphide it may be estimated volumetrically with sufficient accuracy for all practical purposes. Weigh from a quarter to one gram of the slag into the flask (page 46) along with half a gram or so of sulphur-free iron or steel or zinc, moisten the powder with water, heat, and add 20 c.c. hydrochloric acid. The evolved sulphuretted hydrogen is absorbed in zinc acetate, titrated with iodine, and calculated to sulphur as on page 45.

In tabulated analyses the sulphur may be expressed as calcium sulphide or as calcium and sulphur separately; but it is not uncommon to express sulphur as such, and all the calcium as oxide.

**Phosphorus.**—The amount of phosphorus is generally very small and rarely estimated. The sample is opened out with dilute nitric and a few drops of hydrofluoric acid and filtered. The acidity is adjusted with ammonia, nitro-molybdate solution added, etc., as usual.

<sup>1</sup> If not much manganese is present its separation may be omitted, and any oxide accompanying the lime estimated by the bismuthate process and deducted.

**Alkalis.**—The alkalis, chiefly potash, are present in amounts varying from a half to two per cent. They can be determined as in fireclays, but the result is of little value to the furnace manager.

**Titanic Oxide.**—This is a frequent constituent of slags, but it has no metallurgical significance. It is determined by boiling with nitric acid, cooling, and filtering. The filtrate contains most of the titanium. The undissolved portion is added to it after igniting, fusing with sodium carbonate, and digesting with sulphuric acid. The total is estimated colorimetrically.

The crystals of cyano-nitride of titanium, commonly observed in blast-furnace 'bears' may be separated from the slag, according to Reinhardt, by treating the mixture successively with hydrofluoric, hydrofluoric and sulphuric, and sulphuric and chromic acids. The titanium is estimated by fusing with potassium bisulphate, digesting with acidulated water, and precipitating with a small excess of ammonia, followed by a small excess of acetic acid. The formula of the crystals approximates to  $\text{Ti}_5\text{CN}_4$ .

### TAP CINDER.

Puddler's tap cinder may be regarded as a ferrous silicate in which are dissolved various amounts of ferrous and ferric oxides. As the slag or cinder is quite decomposed by hydrochloric acid the analysis is very simple.

**Silica, Iron, Alumina, Lime, and Magnesia.**—Dissolve one and a half grams in the same way as blast-furnace slag, evaporate, collect the silica, and estimate it. Precipitate the iron and alumina in the filtrate with ammonium acetate, make the solution up to 300, and filter off 200 c.c. for the estimation of lime and magnesia in the usual way after separating manganese with bromine and ammonia, or as sulphide.

The residue is dissolved in acid, and one-third of the solution used for the estimation of total iron. The remaining two-thirds is treated like a ferro-aluminium. The precipitate obtained is rarely pure aluminium phosphate; it will contain any chromic or titanic oxides present in the slag as well as traces of vanadic oxide. Chromic and titanic oxide may be determined from this precipitate: the former by titrating the chromic acid after fusing with sodium carbonate or by matching its colour with sodium chromate solutions, and the latter by the hydrogen peroxide test. But such niceties are not generally regarded in works' analyses.

**Sulphur.**—This is estimated gravimetrically as in blast-furnace slags. It exists partly as ferrous sulphide.

**Manganese and Vanadium.**—Manganous oxide is determined as in blast-furnace slags. A little hydrofluoric acid is nearly always needed to complete the decomposition. The presence of a few tenths per cent. vanadic oxide may be observed during the titration by the rapid disappearance of the permanganate tint first formed, and its amount may be roughly estimated during the same operation as on page 89. The peroxide colour estimation can be made only when titanium is absent, and hydrofluoric acid has either not been used or has been completely expelled. The separate estimation of titanous and vanadic oxides is made as in iron ores.

**Ferrous Oxide.**—Dissolve half a gram of the very finely ground slag in hydrochloric acid, and titrate with bichromate. The result is likely to be too high on account of the interference of small particles of iron and ferrous sulphide. The former cannot be removed magnetically, because the cinder itself is more or less magnetic. The ferric iron is represented as usual by the difference between the volume of bichromate needed to titrate the iron existing as ferrous oxide, and the volume needed for the total iron after converting to ferrous oxide.

**Phosphoric Acid.**—Dissolve half a gram of the slag with nitric and hydrofluoric acids, boil off most of the latter, and dilute to 100 c.c. To 25 c.c. (.25 gram) add 12 to 14 c.c. ammonia, and just clear the solution with nitric acid; then add at least twice the usual amount of nitromolybdate reagent and transform the precipitated phosphomolybdate to the lead salt for weighing.

### ACID SIEMENS' SLAG.

These slags are generally insoluble in hydrochloric acid. Fuse one and a quarter grams with two or three grams sodium carbonate, evaporate the dissolved melt with hydrochloric acid, and collect the silica exactly as in a Refractory (page 209). Precipitate the filtrate with ammonium acetate, and estimate the total iron, alumina, lime, and magnesia as in former slags. The separated hydrate or sulphide of manganese may be ignited and weighed, or prepared in previously described ways for the bismuthate estimation.

**Manganese.**—A direct determination of manganous oxide is made by dissolving half a gram of the slag in hydrofluoric and hydrochloric acids, evaporating with sulphuric acid, oxidizing with sodium bis-

muthate, etc., as usual. A mixture of hydrofluoric and nitric acids will sometimes dissolve very finely powdered slags, and thus save the sulphuric acid evaporation, but it is not to be depended on for general use.

**Sulphur.**—Two grams are opened out by fusion with sodium carbonate, the acidified solution of the melt evaporated, the silica eliminated, and barium chloride added to the filtrate after suitably adjusting the acidity with ammonia.

**Phosphorus.**—Decompose two grams with hydrochloric and hydrofluoric acids, evaporate nearly to dryness, transfer to a glass vessel, boil with nitric acid and permanganate, and finish as for an iron ore (page 190).

### BASIC SIEMENS' SLAG.

**Silica.**—Dissolve one and a half grams in hydrochloric acid, evaporate with a little nitric acid, and estimate the collected silica. It should be treated with hydrofluoric and sulphuric acids in order that a small dark-coloured residue, which probably contains chromic oxide, may be fused, dissolved in acid, and added to the following solution :

**Iron and Alumina.**—Neutralize the solution until a slight turbidity forms, add 2 or 3 c.c. acetic acid, and when boiling as much ammonium acetate only as is needed to complete the precipitation of the basic phosphates of iron and aluminium. It is desirable, if not essential, for the completeness of the subsequent separations that all the phosphoric acid should be precipitated; a little ferric chloride should therefore be added if it is feared that bases enough are not already present to effect this. The collected precipitate is re-dissolved and the total iron and alumina determined as in tap cinder. The precipitated aluminium phosphate contains also chromic, titanitic, and vanadic oxides, which may be separated by fusing with sodium carbonate, extracting the melt with water and filtering. Chromic, vanadic, and aluminic oxides are in the filtrate; the residue contains titanitic and traces of manganic and ferric oxides.

**Lime and Magnesia.**—These are determined in a fraction of the filtrate as in blast-furnace slags. The manganese is previously separated as sulphide; if separated with bromine and ammonia a double precipitation is necessary.

**Manganous Oxide and Sulphur.**—These are determined as in tap cinder.

**Phosphorus.**—As in tap cinder. The phosphorus is conveniently precipitated from a portion of the solution intended for the estimation of manganous oxide. If the sample contains ten to twenty per cent. phosphoric acid, a decigram is as much as can be conveniently handled when the yellow precipitate is transformed for weighing into the lead salt. If the final precipitation as ammonium magnesium phosphate and weighing as pyrophosphate is preferred, much larger amounts of the slag may be worked with.

MILL SCALE.

The analysis of this material is accomplished by dissolving the sample in hydrochloric acid and proceeding as though a pure magnetite iron ore were being dealt with. There is no regular demand for analysis of this kind, but the following series by Professor Ledebur are interesting as being perhaps the latest and most complete published :

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Ferric Oxide, -	45.37	42.81	48.74	47.48	39.48	35.97	37.41	51.85
Ferrous Oxide, -	53.62	56.08	50.73	50.77	60.08	63.69	62.32	46.74
Manganous Oxide, -	0.07	0.11	—	0.33	0.43	0.43	—	0.23
Copper Oxide, -	0.01	0.04	—	0.03	0.05	0.03	—	0.01
Silica, -	0.40	0.30	—	1.03	0.00	0.00	—	0.80
Phosphoric Acid, -	0.58	0.25	—	0.04	0.09	0.05	—	0.04
Total, -	100.05	99.59	99.47	99.68	100.13	100.17	99.73	99.67
Metallic Iron, -	73.46	73.90	73.58	72.73	74.37	74.72	74.66	72.64

I. A puddled iron containing 0.08 Mn, 0.25 P. II. and III. puddled irons from different districts. IV. A puddled steel containing 1.42 C, 0.12 Mn, 0.14 Si. V. VI. and VII. are mild basic steels. VIII. A crucible steel containing 0.93 C, 0.13 Mn, 0.31 Si. Scales IV. and VIII. contain respectively 0.17 and 0.16 per cent. alumina.

The ratio of oxygen to iron in the above analyses varies between the limits  $\text{Fe}_7\text{O}_8$  and  $\text{Fe}_4\text{O}_5$ . It is noteworthy that the various impurities pass into the scale in about the same proportion as they exist in the iron, the high silica of IV. and VIII. being probably due to extraneous siliceous material. The complete absence of sulphur from the scale leads to the assumption that it was completely converted into and escaped as sulphur dioxide.

TYPICAL ANALYSES OF SLAGS.

	Blast Furnace Basic Pig Burden.	Puddler's Tap Cinder.	Basic Siemens'.	Acid Siemens'.	Crucible : making Self-hard Steel.
Silica, - - -	33·12	15·90	21·30	60·80	47·96
Alumina, - - -	9·31	0·50	1·92	2·21	16·42
Ferrous Oxide, - - -	0·79	63·14	9·50	18·22	—
Ferric Oxide, - - -	—	5·44	5·16	—	7·92
Manganous Oxide, - - -	3·00	5·31	8·95	9·23	1·81
Lime, - - -	47·98	0·37	37·50	5·01	15·84
Magnesia, - - -	2·06	0·30	4·05	3·60	4·84
Sulphur, - - -	2·21	0·19	0·22	—	—
Sulphuric Acid, - - -	—	—	—	—	0·16
Phosphoric Acid, - - -	0·13	7·68	10·59	—	0·01
Chromic Oxide, - - -	—	0·10	0·25	—	4·30
Tungstic Oxide, - - -	—	—	—	—	0·66
Titanic Oxide, - - -	0·60	0·33	0·30	0·40	—
Vanadic Oxide, - - -	—	0·91	0·47	—	—
Alkalies, - - -	1·00	—	—	—	—
	100·20	100·17	100·21	99·47	99·92

## PART VIII. ANALYSIS OF FUEL.

### I. SOLID FUELS.

#### COAL, COKE, CHARCOAL.

##### **Sampling.**

MORE uncertainty is likely to be introduced through imperfect sampling than is inherent in the analytical processes. Where the crushing has to be done by hand in the time-honoured way there is a tendency to take samples that are too small to represent truck loads of non-homogeneous material. At least a score pieces should be taken or fairly sampled and the whole stamped on an iron plate to the size of a hazel nut, then well mixed and a quarter of the bulk crushed to the size of a pea, and in the same manner a further aliquot portion taken and crushed in an iron mortar. The final sample, passed through a sieve of sixty meshes to the lineal inch, should be kept in a stoppered bottle.

##### **Moisture.**

Moisture is most accurately determined by passing dried air over the coal or coke heated to 110-120° C. and absorbing the water in a weighed calcium chloride or sulphuric acid tube. But the more common, because the more convenient, way is to heat two or three grams in a tared platinum dish at the same temperature.

The weight of the sample decreases for some time and then begins to increase, the lowest weight being generally taken in calculating the percentage of moisture. The increased weight on continued drying is popularly explained by supposing the pyrites, which exists more or less in all coals, is partially oxidized. But the examination of a long series of coals by the chemist to the Iowa Geological Survey points to oxidation of the bitumen of the coal itself as being partly responsible

for the increased weight. The section on "Weathering of Coal" in Percy's *Fuel*, page 289, is interesting in this connection.

### Ash.

A determination which is accurate enough for most works' purposes is made by weighing two or three grams of the coal or coke into a tared platinum dish, placing it in the muffle, and leaving it to take care of itself. Indeed, where large numbers of determinations have to be made, the dishes or crucibles are packed into the hot muffle and left igniting all night.

But Dr. Muck (*Zeit. für Anal. Chemie*, xix. 131)—whose book (*Die Chemie der Steinkohle*: Englemann, Leipzig) may be referred to by those especially interested in coal—has pointed out a number of small errors the ash determination is liable to which should at least be known. These may arise

From the presence of mineral substances, impeding perfect decarbonization, such as phosphates and fusible salts.

From decrepitation.

From the partial volatility of various constituents of the ash, and

From the chemical changes an ash may undergo according to the degree and duration of heat and the supply of air.

Samples are most expeditiously ashed in shallow platinum dishes, although this of course favours the chance of loss through decrepitation and air currents. To minimize these losses the coal should be well powdered and heated very gradually to begin with. This latter precaution, especially in the case of caking coals, prevents the formation of hard coke, the subsequent ignition of which requires a high temperature.

The presence of unburnt coal or coke cannot always be observed by mere inspection. Muck proposed to moisten the ash with alcohol, whereby any unburned particles usually float on the surface. He claims that the ash which previously lay very loosely adheres quite closely to the dish after burning off the alcohol and is more speedily decarbonized. The complete incineration of the carbon may also be assisted, by passing a steady stream of oxygen into the dish, by moistening with ammonium nitrate, or according to Wislicenus, best of all by moistening with dilute hydrogen peroxide. Ashes of coals containing large amounts of pyrites, sulphur, and lime are most difficult to ignite to constant weight.



### Volatile Matter and Coke.

Weigh two grams of the powdered coal into a crucible with a well-fitting lid, and ignite at the mouth of the muffle until the flame of the escaping hydrocarbon gases ceases to be white and nearly disappears; then clasp the crucible in the bow of the tongs, ignite for a minute over a blast lamp, cool in the desiccator and weigh. The loss in weight is counted as volatile matter, the residue is coke.

Comparative estimations should be made always in the same crucible, on the same weight of *undried* coal, and under the same conditions of temperature, etc. Heating over the blast lamp does not decrease the weight of the coke very much if it follows immediately after the hydrocarbon flame has disappeared. If the crucible is first cooled and then blasted, the decrease is very appreciable, as a portion of the coke is burned by the air which meanwhile has gained access to the crucible.

It follows from the last remark that when the volatile matter of coke is being estimated, the ignition for several minutes at a high temperature must consume a portion of the coke itself. This error is allowed for with tolerable exactness by re-heating the cooled and weighed crucible for the same time as before and counting the second loss in weight as equal to the amount of non-volatile coke consumed in the first heating. A more strictly scientific method is to drive off the volatile matter in a current of nitrogen (Meade and Attix).

### Sulphur.

Sulphur exists in coal in at least three different states: as sulphide, as sulphate, and as an organic compound. The estimation of total sulphur only is commonly made use of for works' purposes, although there is much to be said for a discrimination between 'combustible' sulphur and that remaining in the ash.

*Total Sulphur.*—One gram of the powdered coal or coke is shaken in a stoppered bottle with three grams of the following mixture:

Lime, . . . . .	160 grams.
Potassium Carbonate, . . . . .	20 grams.
Sodium Carbonate, . . . . .	20 grams.

and after transferring to a platinum crucible covered with one additional gram of it. The crucible is then heated in the muffle and stirred occasionally with a platinum rod until the fuel appears to be completely burned.

Empty the contents of the crucible into a beaker, add about 70 c.c. water, a few drops of bromine to oxidize any sulphite which may have

formed, and a small excess of hydrochloric acid. Although on boiling everything may appear to be dissolved, it is as well to pour through a small filter before adding barium chloride. The barium sulphate is collected and weighed as usual, and any required correction made for sulphur in the reagents.<sup>1</sup> Determinations of sulphur and ash must not be carried on in the same muffle, as the lime of the former absorbs some of the sulphur dioxide evolved from the latter.

*Sulphate Sulphur.*—Of the different forms in which sulphur exists in coal this only can be determined directly. The process described by Calvert before the British Association in 1871 is the one generally used. Calvert insisted that it was “most important from a metallurgical point of view to give the sulphate figure separately, because the sulphur combined with calcium as sulphate will not leave its stronger base to deteriorate the quality of the iron, either in the blast furnace or in any of the subsequent processes of manufacture.”

Boil the finely powdered coal or coke and an equal weight of sodium carbonate with 300 c.c. water for 24 hours. The residue is filtered off and rapidly washed with boiling water. The filtrate is oxidized with a little bromine and hydrochloric acid, and the sulphuric acid determined as usual. Dr. Drown objects to this means of estimating calcium sulphate, on the ground that sodium carbonate readily attacks pyrites; even water when heated in contact with pyrites in the air contains notable quantities of sulphuric acid. Drown suggests that the calcium sulphate should be dissolved out by means of water with careful exclusion of air.

*Sulphide Sulphur.*—The following process was suggested by Drown (*Amer. Inst. Mining Engineers and Chem. News*, xliii. 89). Saturate a solution of caustic soda of 1.25 specific gravity with bromine, and add a little more soda, so that free bromine may not be given off. Moisten one or two grams of the finely powdered coal with 10 c.c. of this solution, heat, and then add hydrochloric to a faintly acid reaction. Two more

<sup>1</sup> Lime made from good specimens of marble is almost free from sulphur. Two grams of the Eschka mixture—magnesia with half its weight of anhydrous sodium carbonate—may be used instead of that given if magnesia nearly free from sulphur can be obtained. N. W. Lord gives the following method of purifying light calcined magnesia. Add about two per cent. of pure sodium carbonate and stir up with enough boiling water to make a thin liquid. Boil the mixture a few minutes, allow to settle, and decant off the clear liquor. Repeat this operation and continue the washing by decantation until the liquid, after being acidified with hydrochloric acid, shows no trace of sulphates when treated with barium chloride. The magnesia is then poured on to a large filter, drained, and finally ignited.

additions of the alkaline solution of 20 c.c. each are made at intervals of ten minutes, each addition being followed by hydrochloric acid. The hot solution is then evaporated to dryness, the dry mass taken up in hydrochloric acid, silica eliminated, and the sulphur precipitated with barium chloride.

The coal as such is not attacked, and therefore the sulphur obtained represents that existing as pyrites and as sulphates. The difference between the total sulphur and that just determined is the

*Organic Sulphur.*—This form of sulphur and that existing as sulphide may be determined by heating the coal at low redness in a current of oxygen and collecting the volatile products in brominized hydrochloric acid.

Since it was recognized that sulphur in coals could be organically combined, the practice of estimating total sulphur by digestion with strong oxidizing reagents such as aqua regia, hydrochloric acid and potassium chlorate, etc., has been discontinued. Proof of the existence of organic sulphur is furnished by the following observations :

When coal is heated in a closed tube, gaseous and liquid products containing sulphur are evolved at a temperature considerably below that at which iron pyrites is decomposed, or free sulphur volatilized.

The analysis of some coals shows an excess of sulphur over the quantity, which all the iron present would require to form disulphide and all the bases to form sulphates.

#### Arsenic.

It has been known for many years that some coals contain decided traces of metals, such as copper, lead, arsenic, and antimony. The epidemic of arsenical poisoning in Manchester and district in 1900 caused special search for arsenic to be made in all kinds of materials used for brewing purposes. This emphasised the presence of arsenic in coal and coke, and caused several methods for its determination to be proposed.

It is unlikely that the amount of arsenic existing in fuels will in any way prejudice their uses for iron and steel-making purposes. Such analysts as are interested in colliery and coking plants, whose produce is otherwise used, will find several means of making the assay described in the journals for 1901 : particularly *Journal Soc. Chem. Industry* :<sup>1</sup> and the *Analyst*.

<sup>1</sup> The papers and abstracts which have appeared in this journal as well as extracts from other journals are published separately (Eyre and Spottiswoode : ls.).

## ANALYSIS OF THE ASH.

**Sulphur.**—Three grams of the fuel are ashed, the residue dissolved in hydrochloric acid—*via* sodium carbonate fusion if necessary—and the sulphur precipitated with barium chloride as usual. The proportion of the total sulphur found in the ash is a variable quantity.

**Phosphorus.**—All the phosphorus present in the coal remains in the ash. It may vary in amount from traces up to three per cent., and practically the whole of it passes into the pig-iron when used in the blast-furnace.

The ash from five to ten grams of coal or coke is dissolved in hydrochloric and hydrofluoric acids and evaporated to fumes with a small amount of sulphuric acid. Now add 20 c.c. 1·20 nitric acid with a pinch of pure bar iron dissolved in it, and ammonia until the red colour of ferric oxynitrate shows that all the free acid is neutralized. Then add 50 c.c. nitro-molybdate reagent, and estimate the precipitated phosphomolybdate as usual.

The remaining constituents—lime, magnesia, ferric oxide, and alumina—are estimated as in refractory materials.

## ULTIMATE ANALYSIS.

**Carbon and Hydrogen.**

A long dry glass tube is drawn out at one end and covered with asbestos over the part to be heated, with the exception of a small space in the neighbourhood of the boat. For three or four inches of its length it is packed with well-ignited granular oxide of copper. Before making the pending assay the tube is heated, and two or three litres of dried air drawn through into a weighed calcium chloride tube so as to ensure the absence of moisture.

A quarter of a gram of the coal or coke is mixed with two and a half grams of perfectly dry lead chromate, transferred to a boat, and placed in the tube. A current of dry air or oxygen is passed, and the lights turned up underneath the boat one by one. When the combustion appears to be complete, and all traces of moisture have been driven forward, the tared calcium chloride tube and potash bulb are separately re-weighed, and the percentage of hydrogen and carbon calculated from the increase. Thus:

( $\text{H}_2\text{O}$  absorbed in  $\text{CaCl}_2$  – that due to moisture)  $\times 0.1111$  equals the weight of hydrogen in the coal taken, and

$\text{CO}_2$  absorbed by KHO bulb  $\times 0.2727$  equals the weight of carbon in the coal taken.

The respective percentages of carbon and hydrogen are reliable only when it is certain that the fuel contains no carbon dioxide, gaseous or as calcium carbonate, and no water other than that driven off under the conditions of moisture determinations. Dr. Percy remarks (*Fuel*, page 310): "It is certain that the alumina in ashes must either wholly, or in great measure exist in combination with silica as clay; and clay holds water in combination which cannot be expelled at a temperature far more than sufficient to decompose coal."

### Nitrogen and Oxygen.

Nitrogen may be determined in finely powdered coal by Dumas' (absolute) method, Varrentrap & Wills' (soda-lime) method, or the Kjeldahl method.

Schmitz (*Stahl und Eisen*, vi. 47) has made a special study of these modes of determining nitrogen in coal and coke. He objects to Dumas' method, because it is difficult to manipulate, and neither coal nor coke are completely burned under the circumstances, even after four or five hours' heating. The soda-lime method he finds to give low results with coal, and to be quite unsuitable for use with coke. The following modified form of the Kjeldahl method is recommended:

From 0.8 to one gram of very finely powdered coal or 0.5 to 0.7 gram of coke are placed in a quarter litre flask along with a gram of powdered mercuric oxide and 20 c.c. concentrated sulphuric acid; the whole is then heated and kept rapidly boiling for from two to three hours. All varieties of coal, even anthracite, will be in solution at the end of this period. The contents of the flask are allowed to cool, and then poured into a distillation flask containing some cold water; then 100-120 c.c. caustic soda solution of 1.25 specific gravity are added, and also 35 c.c. of a solution of yellow sodium sulphide containing about 40 grams per litre. Finally, a small piece of zinc is added to prevent bumping, and the liquid boiled for about twenty minutes. The ammonia is absorbed in 20 to 30 c.c. of a standard sulphuric acid solution, and the excess is titrated with standard baryta water, rosolic acid being used as indicator. An arrangement for collecting any drops of liquid carried over is introduced between the distilling flask and condenser.

Coke is treated with the same quantities of mercuric oxide and sulphuric acid as coal, except that at the end of one hour's boiling an

extra gram of mercuric oxide is added little by little, and in a similar manner two grams of finely powdered potassium permanganate are added when the solution is at a rapid boil. It is necessary to shake frequently so as to wash down the particles of coke which rise and adhere to the sides of the flask. As two grams of mercuric oxide are used it is also necessary to use twice the quantity of sodium sulphide solution. The distillation and titration are made as before.

Oxygen is generally determined by difference, about one half only of the sulphur being reckoned. Some more or less satisfactory methods for making direct determinations are given in the second volume of Fresenius' *Quant. Analysis*.

#### TYPICAL ANALYSES.

	Beechwood Charcoal.	Coal Totley.	Cannel Coal Totley.	Coke.	Coke Denaby.
Coke, - - -	—	68·00	72·10	—	—
Volatile, - - -	—	32·00	27·90	—	—
Ash, - - -	3·02	0·92	7·13	8·52	6·85
Sulphur, - - -	—	0·69	2·22	1·03	0·62
Water, - - -	7·23	4·02	1·96	1·38	—
Carbon, - - -	85·89	77·72	75·00	87·60	92·29
Hydrogen, - - -	2·41	5·18	4·53	0·25	—
Nitrogen, { - - -	1·45	{ 1·27 }	9·16	1·20	—
Oxygen, { - - -		{ 10·20 }			
	100·00	100·00	100·00	100·00	99·76
Analyst - - -	Faisst <sup>1</sup>	Authors	Authors	Bell	Authors

<sup>1</sup> The composition of charcoal when made from the same wood varies greatly according to the temperature at which carbonization is effected.

## II. GAS ANALYSIS.

The complete analysis of blast furnace gas and of producer gas for open-hearth furnaces may involve a determination of carbon dioxide, oxygen, nitrogen, hydrogen, carbon monoxide, methane, and ethylene. Of these, the carbon dioxide, oxygen, carbon monoxide, and ethylene may be determined by direct absorption, one at a time, with suitable solvents. The hydrogen and methane can then be exploded with a measured excess of oxygen, and their amounts determined from the contraction

due to the explosion and from the amount of carbon dioxide formed. The nitrogen is obtained by difference. It is obvious that carbon monoxide may also be estimated by combustion along with the methane and hydrogen, but a determination of the excess of oxygen by explosion with hydrogen then becomes necessary.

*Case 1. Carbon monoxide previously removed by absorption.*

Let  $x$  = amount of hydrogen  
 $y$  = amount of methane  
 $a$  = measured contraction due to explosion  
 $b$  = measured amount of carbon dioxide formed.

Then 
$$\frac{3}{2}x + 2y = a$$
  

$$y = b.$$

*Case 2. Carbon monoxide present.*

Let  $x$  = amount of hydrogen  
 $y$  = amount of methane  
 $z$  = amount of carbon monoxide  
 $w$  = amount of nitrogen  
 $a$  = amount of oxygen added for combustion  
 $b$  = contraction due to explosion  
 $c$  = amount of carbon dioxide formed  
 $d$  = total volume of gas after absorbing carbon dioxide  
 $e$  = contraction due to explosion of  $d$  with excess of hydrogen.

The volume  $d$  is made up of the nitrogen and the excess of oxygen, and this latter is evidently  $\frac{1}{3}e$ , so that  $w = \text{Nitrogen} = d - \frac{1}{3}e$ .

Now 
$$b = \frac{3}{2}x + 2y + \frac{1}{2}z \dots \dots \dots (1)$$

$$c = y + z \dots \dots \dots (2)$$

The contraction  $e$  after exploding with hydrogen is made up of the surplus oxygen and twice its volume of hydrogen, so that we have

$$\text{Surplus oxygen} = a - \left( \frac{1}{2}x + 2y + \frac{1}{2}z \right)$$

and

$$e = 3a - 3 \left( \frac{1}{2}x + 2y + \frac{1}{2}z \right)$$

$$\frac{3}{2}x + 6y + \frac{3}{2}z = 3a - e \dots \dots \dots (3)$$

The solution of the equations (1) (2) and (3) yields

$$\text{Hydrogen} = x = b + \frac{1}{3}e - a$$

$$\text{Methane} = y = a - \frac{1}{3}(b + c + e)$$

$$\text{Carbon Monoxide} = z = \frac{1}{3}(4c + b + e) - a.$$

### Stead's Gas Apparatus.

The number of different forms of apparatus for gas analysis is legion, and almost any one of them will yield satisfactory results when certain conditions are observed. A description of Stead's form, which is easily and rapidly manipulated, is appended.

It consists essentially of a vertical graduated tube *A* (Fig. 15), in which all measurements are made, and to which access is given at the upper end by means of two taps *B* and *C* fitting a horizontal capillary tube. The lower end of *A* is connected with a similar ungraduated tube *D*, and the two of them by means of a T-piece and indiarubber tubing with the mercury reservoir *E* which can be raised or lowered by means of the weight *F*, to which it is connected by strong cord passing over pulleys. The upper end of *D* is open to the atmosphere at *H*, so that the whole arrangement permits the readings to be taken at atmospheric pressure by adjusting the mercury columns to the same level in *A* and *D*. A sliding spirit level facilitates this adjustment. The tap *B* effects communication between *A* and the laboratory vessel *G* used for absorption. The explosions are effected by sparking between the platinum wires fused into the glass at the upper end of *A*. The whole apparatus is elegantly and safely supported by a wooden framework standing in a tray (not shown in the figure) to provide against accidental loss of mercury.

### Sampling.

When it is necessary to instantaneously take a sample of gas for analysis, one of the laboratory vessels referred to above (*G*) and shown separately in Fig. 16 may be conveniently used. The cylinder contains mercury, and this is sucked up into the laboratory vessel, past the stop-cock to the top of the capillary tube. The tap is then closed. A charred cork, carrying a piece of glass tubing, is inserted in the sampling hole, and when the gas issues freely, connection is made between the end of the glass tubing and the laboratory vessel by means



of thick-walled indiarubber tubing. On opening the tap, the fall of the mercury aspirates sufficient gas for two analyses if the amount of mercury in the cylinder is not too large.

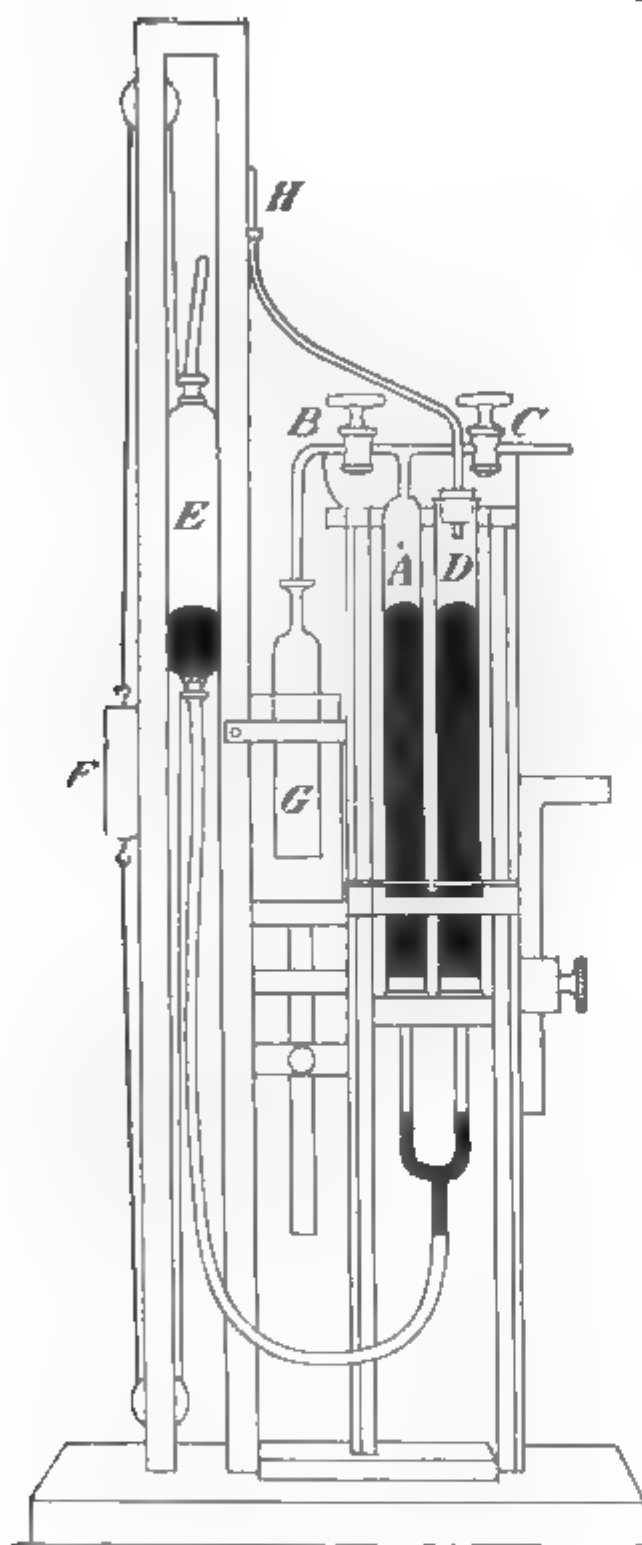


FIG. 15.



FIG. 16.

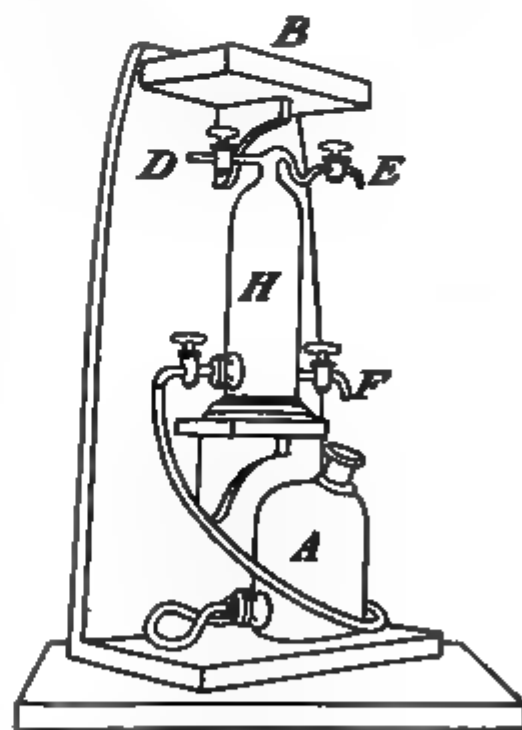


FIG. 17.

When it is desirable to make the collection of a sample of gas extend over some considerable time, Stead's sampling apparatus is particularly useful. It consists (Fig. 17) of the gas receiver *H* provided with two taps, *E* and *D*, at its upper end, and other two, *C* and *F*, at the lower. The tap *C* is connected with a mercury reservoir *A*. In sampling, the

whole arrangement is hung on the side of the flue, and the mercury reservoir placed on the shelf *B*, whilst the taps *C* and *D* are open. In this way the receiver is filled with mercury, whereupon *C* is closed and the reservoir lowered. The end *E* is then connected with the flue and the gas allowed to displace any air from the capillaries by keeping *D* open. After closing *D*, the mercury reservoir *A* is placed under the tap *F*, which is then opened. It is obvious that the rate at which the gas is aspirated is determined by the rate at which the mercury is allowed to flow. This can be regulated so as to make the sampling extend over a pre-determined period of time. In order to prevent the capillaries from becoming choked, the end of the tube inserted in the flue should be covered with asbestos, over which a piece of copper gauze is placed.

#### Analysis of the Gas.

The laboratory vessel *G* (Fig. 15) containing caustic potash must first of all be freed from air. This is done by closing the tap *C* and opening *B*, the mercury reservoir being slowly and carefully lowered until the potash reaches the tap *B*, which is then quickly closed. Some practice is required to effect this operation in the least possible time, without carrying a drop or two of the potash solution into *A*. The tube *A* now contains the air thus carried over from *G*, and in order to expel it the tap *C* is opened, and the mercury reservoir raised until all the air is expelled and mercury just drips out. The apparatus is now ready for the analysis.

#### I. *Rapid Analysis.*

Blast furnace gas contains little or no methane or oxygen, and the amount of the former in producer gas amounts to a few per cents. only, so that its elements may be returned as carbon monoxide and hydrogen, whilst oxygen exists in traces only. The analysis thus involves a determination of carbon dioxide, carbon monoxide, hydrogen, and nitrogen.

If the sample has been collected in a laboratory vessel, place this on the support, and after filling up the indiarubber tubing with mercury, connect it at the end of *C* and aspirate 80 to 100 volumes of the sample. Level up after closing *C* and measure. Next, keeping *C* closed and opening *B*, transfer the gas to the potash laboratory vessel by lifting the reservoir until mercury drips over. Close *B* and sweep out the gas in the capillary to the right by opening *C*. Absorption of the carbon dioxide is complete in about three minutes, and the gas may be carried back into *A* as explained above. After measuring,

introduce an excess of pure oxygen from a laboratory vessel in the same fashion as the sample of gas was taken. Level, measure, and explode. After cooling, level up and measure again, and determine lastly the amount of carbon dioxide formed by the explosion by making another absorption in potash. Then if

$x$  = hydrogen,       $y$  = carbon monoxide,

$a$  = contraction after explosion,

$b$  = contraction after absorbing carbon dioxide formed,

$$\frac{3}{2}x + \frac{1}{2}y = a$$

$$y = b,$$

whence

$$x = \frac{2}{3}\left(a - \frac{1}{2}b\right).$$

*Example.*

#### PRODUCER GAS.

Carbon Monoxide, -	-	24.7
Hydrogen, -	-	10.5
Carbon Dioxide, -	-	3.5
Nitrogen, -	-	61.3
		100.0

#### II. Complete Analysis.

The authors have obtained the best results with Stead's apparatus by absorbing *all* absorbable gases before resorting to a combustion. The simple form of apparatus (Fig. 15) is in such cases rather inconvenient, because it necessitates a cumbersome method of changing the absorption vessels. Stead describes (*Journ. Soc. Chem. Ind.* 1889, 178) an arrangement of six vessels, which can, by means of a turn-table, be brought one at a time in connection with the eudiometer, the inconvenience mentioned above being thereby overcome. The authors have received a sketch of a still later form of absorption vessel as used by Mr. Stead, and having found it eminently satisfactory, append, through the kindness of that gentleman, a short description (see Fig. 18).

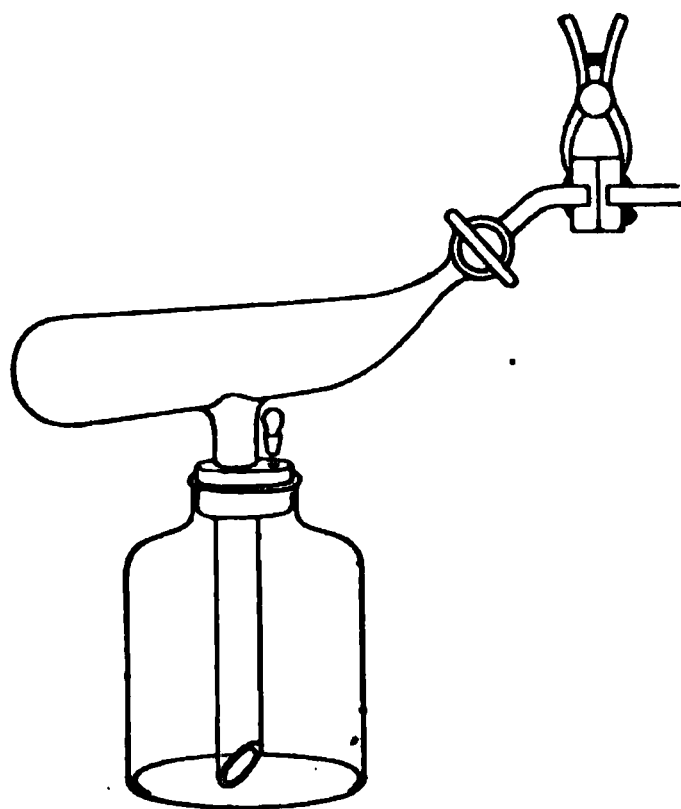


FIG. 18.

The solution is contained in a glass bottle closed by a rubber bung which carries a small glass stopper and a pipette furnished with a tap. The mode of connection with the limb of the gas apparatus is similar to the one described in the paper just alluded to. The ends of each absorption-vessel tube and that of the limb of the gas apparatus are securely fastened to square pieces of ground glass by means of electricians' cement, which is applied to the parts after warming. A clamp holds the greased faces of the glass plates in position whilst the gas is being transferred one way or the other. It will be seen that each vessel is easily detached and allows of vigorous shaking at the same time that a considerable surface area of liquid is presented to the gas. In this way the rate of absorption of such gases as carbon monoxide is considerably increased.

The mode of conducting the analysis is as follows :

- (a) Absorb carbon dioxide with caustic potash.
- (b) Absorb oxygen with solution of pyrogallol in caustic potash. This may frequently be omitted, or, as an alternative, this solution may be used for absorbing the carbon dioxide and oxygen together.
- (c) Absorb carbon monoxide in cuprous chloride dissolved in hydrochloric acid, and before measuring the gas left, pass it into the potash bottle to remove traces of hydrochloric acid vapour.
- (d) Absorb ethylene in fuming sulphuric acid, and before measuring pass it into potash for a short time. This determination may generally be omitted.
- (e) The remaining gas consists of hydrogen, methane, and nitrogen. Add excess of oxygen, explode, measure after cooling, pass into potash to absorb carbon dioxide formed, and measure again. Calculate results according to instructions on page 243.

ANALYSES OF 'PRODUCER' GASES.

	I.	II.
Carbon Monoxide, - - -	22·8	24·6
Methane, - - - -	4·2	5·0
Hydrogen, - - - -	10·2	9·7
Carbon Dioxide, - - -	3·5	4·2
Nitrogen, - - - -	59·3	56·5
	100·0	100·0

**Reagents for Absorption.**

*Caustic Potash.*—Dissolve 60 grams of the commercial article in 200 c.c. water.

*Alkaline Pyrogallol.*—Dissolve 20 grams of pyrogallol in 200 c.c. of the above potash solution.

*Cuprous Chloride.*—Dissolve 30 grams of the solid in 50 c.c. of water and 150 c.c. strong hydrochloric acid. The dark coloured solution obtained should be kept in a tightly-corked bottle in contact with a strip or two of metallic copper. It gradually becomes colourless.

**General Remarks.**—The graduated tube of the Stead apparatus is readily cleaned when necessary by introducing dilute hydrochloric acid and afterwards water. This may be found necessary during an actual analysis if a drop of potash solution has been accidentally carried over from the absorption bottle, for in such a case it will be found difficult, if not impossible, to effect sparking. The analysis need not be lost, for the cleansing can be accomplished whilst the gas lies in one of the absorption pipettes.

Pure oxygen for explosions is easily made from potassium chlorate. A bulb of about an inch in diameter is blown on the end of a piece of quarter inch glass tubing, and after introducing the powdered salt, the tube is drawn out and bent into the form shown in Fig. 19.

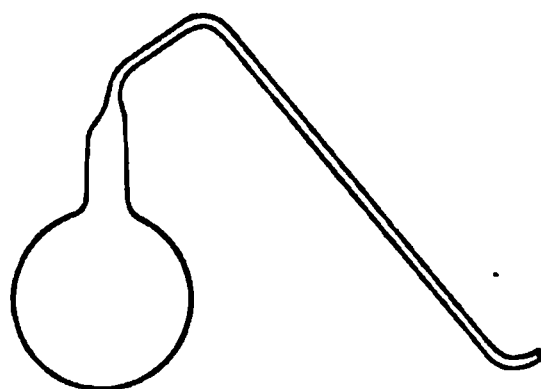


FIG. 19.

## PART IX. THE ANALYSIS OF BOILER WATER, BOILER SCALES, Etc.

THE authors cannot claim to have had very much practical experience of the technical analysis of boiler waters and boiler scales, so that some of the subject matter of this chapter partakes more of the character of a compilation than is desirable in a work in which, as a whole, only those processes which have been extensively practised by the authors are described.

The analysis of boiler water, for technical purposes, primarily involves a determination of the mineral matter capable of forming a deposit on the boiler plates. The principal scale-forming ingredients of water are salts of calcium and magnesium. Stillman has, however, pointed out the importance of the determination of the alkali metals, although of course their salts cannot be considered as scale-formers. This arises from the fact that if the water does not contain sufficient chlorine to 'fix' these metals as chlorides, the excess of sodium or potassium will be in union with the sulphate radicle, an equivalent diminution in the amount of scale-forming calcium sulphate resulting.

Water supplied to boilers does not usually contain any substance likely to attack the plates whilst it remains in solution ; free acid must of course be neutralized, and neutral metallic salts in general have little action on steel at working temperatures and pressures. To this statement there is the well-known exception of magnesium chloride, which, even in the absence of air, attacks iron at the boiling-point of water (A. Wagner). The usually-accepted explanation of the corrosion by magnesium chloride is that this compound is readily hydrolyzed with formation of free hydrochloric acid.

## THE COMPLETE ANALYSIS OF BOILER WATER.

**Total Solids.**—A measured volume (a litre will generally provide sufficient solid residue for its complete analysis) of the sample is evaporated to dryness over the water bath in a weighed platinum dish. The residue is dried to constant weight at 105°-110° C.

The readiness with which magnesium chloride decomposes, and the difficulty with which the complete expulsion of water of crystallization from calcium sulphate and chloride is effected, make the results of this estimation unreliable when these substances are present in large amounts. As the dried residue is nearly always very hygroscopic, Mason recommends the evaporation of the sample in a weighed flask of about 100 c.c. capacity. The flask is provided with a stop-cock instead of the usual glass stopper, the latter, after cooling, being sometimes difficult to dislodge.

**Organic Matter and Carbon Dioxide.**—The 'total-solids residue' is gently ignited over a bunsen flame, finishing at a red heat. The loss of weight represents organic matter and carbon dioxide.

Some analysts prefer to determine the carbon dioxide separately by first re-carbonating the residue obtained on ignition, so as to obtain the total 'fixed' solids, and then decomposing a portion of this new residue with acid, the evolved carbon dioxide being estimated by means of one of the many forms of apparatus for this purpose.

**Iron, Alumina, Lime, Magnesia, Silica, etc.**—The 'total-solids' residue is exhausted with a mixture of equal parts of hydrochloric acid and water, and the solution filtered into a graduated flask.

A portion of the filtrate, after making up to the mark, is precipitated with ammonia, the ferric oxide and alumina filtered off, ignited, and weighed together. In the filtrate from these, the calcium is precipitated as oxalate and weighed as lime. The filtrate from the calcium oxalate is transferred to a weighed dish and evaporated to dryness with a slight excess of sulphuric acid. Ignition to constant weight gives sulphates of magnesium, potassium, and sodium. The mass is extracted with water, and the magnesium precipitated from half the solution and weighed as pyrophosphate. In the other half the potassium is determined as potassium platonic chloride, and the sodium obtained finally by difference.

The other portion of the filtrate is precipitated with barium chloride, and the resulting barium sulphate estimated as usual.

The residue, after ignition, may contain silica, ferric oxide, alumina,

and possibly calcium sulphate. It is fused with sodium carbonate, extracted as usual with hydrochloric acid, evaporated to dryness, baked, and the silica determined as usual. The filtrate is examined for iron, aluminium, and calcium, and the amounts found added to those already found in the original filtrate.

**Chlorine.**—This is determined in a fresh sample of the water by means of a standard silver nitrate solution,<sup>1</sup> using potassium chromate as an indicator.

### TABULATION OF THE RESULTS.

It is customary to unite the anions and kathions by calculation according to the following scheme :

(a) The 'chlorion' is combined with the sodium, and if in excess, with potassium, magnesium, and calcium, in the order named.

(b) The 'sulphation' is combined with any alkali left uncombined by the chlorine, and then with calcium and magnesium.

(c) The carbon dioxide, after the combinations (a) and (b) have been made, is finally linked with calcium and magnesium.

### RAPID SCHEMES FOR THE ANALYSIS OF BOILER WATER.

A rapid approximate analysis of boiler water will often be found sufficient for most purposes, and there are several such schemes.

For example, the solid residue obtained by evaporation of a measured volume of the water may be extracted with a mixture of equal parts of alcohol and water, and, without further analysis, the residue may be regarded as 'scale-forming material.' Again, after weighing the total solid residue, this may be re-carbonated, ignited, and weighed, thus yielding the total mineral matter, and by difference the organic matter. Extraction of the residue with water then yields by difference the total scale-formers of which, if necessary, a systematic analysis may be made. The second of these schemes would evidently be grossly inaccurate if, after ignition, the solubility of calcium sulphate in distilled water were appreciable. The fact that it is not has been amply proved by Main.

As the most important and dangerous constituents of boiler water

<sup>1</sup> A solution of decinormal strength is made by dissolving 16.966 grams of silver nitrate crystals and making up to a litre.



are salts of magnesium and calcium, a rapid scheme for their determination is of value, more particularly as such a determination would yield information sufficient to make possible their almost complete removal from the feed water by precipitation. With a view to this, Kalmann's method for the technical analysis of boiler water consists in the determination of

- (1) *Combined Carbon Dioxide*—by titration with decinormal acid ;
- (2) *Calcium*—by precipitation as oxalate without previous removal of silica, iron, and aluminium ;
- (3) *Magnesium*—as pyrophosphate in the filtrate from the calcium.

For the same reason, brief descriptions of the methods for the determination of the 'hardness' of water are appended. More detailed instructions will be found in books dealing with water analysis.

## HARDNESS OF WATER.

### I. *Hehner's Process.*

This consists in the determination of calcium and magnesium carbonates (temporary hardness) by titration with a standard solution of sulphuric acid. The sulphates of these two metals (permanent hardness) are then determined by adding excess of standard sodium carbonate, boiling for about half-an-hour to precipitate the carbonates, and titrating the excess of alkali. If magnesium sulphate is present, the solution must be evaporated to dryness and the titration performed on an aqueous extract of the residue.

Results are usually expressed in parts of calcium carbonate per 100,000 of the water.

*Temporary Hardness.*—500 c.c. of the water are titrated with decinormal sulphuric acid, using methyl orange as an indicator

$$1 \text{ c.c. } \cdot \frac{N}{10} \text{H}_2\text{SO}_4 = 0.005 \text{ gram CaCO}_3.$$

*Permanent Hardness.*—250 c.c. of the water are boiled for half-an-hour (or, if magnesium sulphate is present, are evaporated to dryness) with 50 c.c. decinormal sodium carbonate. After filtering (or extracting with freshly boiled distilled water) and making up to 250 c.c., the excess of sodium carbonate is determined on a fraction by means of the standard acid.

### II. *Clark's Process.*

This process, which appears to be rapidly and not undeservedly growing obsolete, consists in precipitating the calcium and magnesium

salts by means of a solution of soap which has been previously standardized against a prepared solution of calcium chloride.

*Standard Solution of Calcium Chloride.*—This is made by dissolving 2 decigrams of pure Iceland spar in a small quantity of hydrochloric acid, evaporating several times to dryness in order to expel every trace of acid, and making finally up to one litre with distilled water.

*Standard Soap Solution.*—This is conveniently made by dissolving about 80 grams of pure oleic acid in alcohol and adding pure potassium hydrate until a permanent pink tinge is just imparted to the solution, to which a few drops of a solution of phenol phthalein have been previously added. The solution of potassium oleate thus made will be too strong, and must be diluted until 50 c.c. of the standard calcium chloride solution require exactly 14.25 c.c. of the soap solution. The titration is performed thus :—50 c.c. of the calcium chloride solution are transferred to a stoppered bottle, the pipette being allowed to drain without blowing through it. The soap solution is run in from a burette, a cubic centimetre at a time at first, shaking well after each addition, and towards the finish in much smaller amounts. The end point, which is easily discerned after a little experience of the sound produced on shaking, is reached when a lather is obtained which persists on the surface for five minutes after placing the bottle on its side.

*The Operation.*—50 c.c. of the sample of water are put in the stoppered bottle and vigorously shaken, any expelled carbon dioxide being then sucked out. The total hardness is then determined by means of the standard soap solution in the manner just described. The permanent hardness is obtained by well boiling a sample to precipitate carbonates, freshly boiled distilled water being added from time to time to make up loss by evaporation, diluting to original volume after cooling, filtering through a dry paper, and titrating a measured fraction of the filtrate with the soap solution.

The results in degrees of hardness are read off from Clark's table, which will be found on page 349. Reference to it will show that no provision is made for hardnesses exceeding 16 degrees. With waters of greater hardness a suitable fraction of 50 c.c. is taken in the first instance and made up to 50 c.c. with distilled water.

The end point in the Clark process is difficult to hit when magnesium salts are present in predominating amounts, as they react much more slowly with the soap. This fact is, by some practised operators, actually taken advantage of, the almost complete precipitation of

calcium oleate before that of the magnesium salt begins furnishing a rough approximation to the quantities of both metals.

Throughout the soap test, dilution with *recently-boiled* distilled water is imperative; on standing, it absorbs an appreciable quantity of carbon dioxide.

### BOILER SCALES.

The analysis of a boiler scale presents no difficulty. Many scales may be opened out with hydrochloric acid, leaving a small siliceous residue, which may be weighed as silica. If not readily attacked by acids, the ordinary fusion mixture may be used and the analysis conducted as for a refractory material (*q.v.*).

The results of the analysis should not be taken as a basis for judging the character of the water. The same figures are seldom yielded by two samples of scale taken from different parts of the same boiler, whilst their composition is necessarily influenced to some extent by the means adopted for preventing their formation.

When calcium sulphate is the predominating constituent, the scale is usually very hard, and often possesses a distinctly vitreous appearance. When first deposited this substance is probably hydrated, but contact with the hot plates removes the water of crystallization, and bakes the anhydrous salt into a hard coherent mass.

When the chief constituent of a boiler scale is calcium carbonate, the scale is not so hard as in the case of sulphate. The hardness, however, is very variable, and would appear to be influenced considerably by the minor constituents.

Ridenour (*Chem. News*, lxxxiv. 191) is of opinion that when a scale contains much silica, this exists as calcium silicate, and he attributes its formation to the decomposition of calcium carbonate by free silicic acid under the existing conditions of vigorous boiling under pressure. Considerable support is furnished to this view by the existence of calcium carbonate in the feed water and its absence in the scale.

Magnesia scales, which do not present any marked physical character, may consist of oxide, hydrate, or carbonate. Contact with the hot plates may result in removal of carbon dioxide from the carbonate, and this action may be followed by a partial or complete dehydration of the hydrate. It seems to be generally agreed that magnesium hydrate is an extremely common constituent of boiler scales formed from magnesian waters. A determination of the combined water in a boiler scale should accordingly not be forgotten.

The presence of zinc in boiler scales need occasion no alarm, as alkaline solutions of this metal are frequently used as anti-incrusting agents.

### Prevention of Scale Formation.

A very large number of substances has been used for the prevention of scale formation. Exclusive of the innumerable compositions that have been placed on the market from time to time, such substances as tannic acid, caustic soda, tallow, potatoes, ammonium chloride, etc., have been used. In this connection attention is directed to the statement by Doremus (*Chem. News*, lxix. 5) that the addition of sodium fluoride causes the rapid precipitation of the fluorides of the alkaline earthy metals in the form of a loose amorphous powder. If fed continuously, one-fourth of the theoretical amount of sodium fluoride is stated to be amply sufficient for the prevention of scale, whilst its admission to the boiler rapidly loosens old scales.

The best and most scientific treatment of the boiler water, however, consists in the precipitation of the calcium and magnesium salts outside the boiler. It is beyond the scope of this work to deal with the many mechanical contrivances for the rapid deposition and filtration of the precipitated materials from the feed water before its admission to the boiler, but the authors deem it advisable to explain at some length the determination of the necessary amounts of the precipitants used.

Dr. Clark was apparently the first to recommend the addition of lime in quantity sufficient to precipitate the combined carbon dioxide, but this evidently does not account for the sulphates of calcium and magnesium. Since that time, 1841, this subject has engaged the attention of many workers, and the general result of their labours has been the adoption of sodium carbonate, slaked lime, and caustic soda as precipitants. The addition to these, or to a mixture of them, of a small quantity of alum to facilitate the deposition of organic matter, suffices to reduce the quantity of scale-forming material to a minimum.

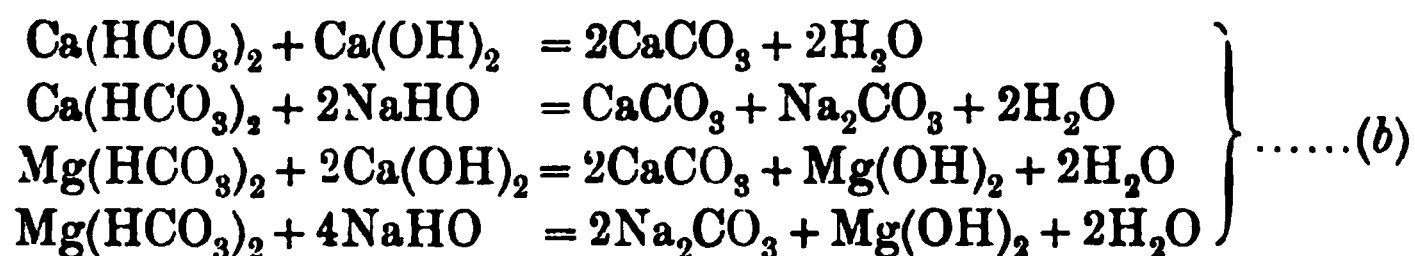
The following treatment of this matter is substantially an account of Kalmann's paper on Béranger and Stingl's method of softening water. The paper is excellently abstracted in the *Journ. Soc. Chem. Ind.* 1890, 1065.

The magnesium and calcium salts are classified into three groups :

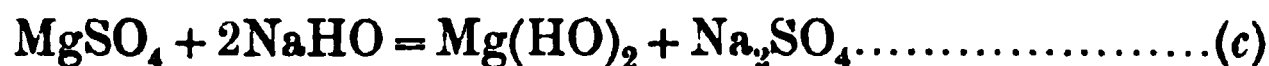
I. *Calcium Salts other than Bicarbonate*.—These are precipitated with sodium carbonate, one molecule of which is required for every molecule of such calcium salt.



II. *Bicarbonate of Calcium and Magnesium.*—These are removed by calcium or sodium hydrate, separately or together.



III. *Magnesium Salts other than Bicarbonate.*—These are removed by caustic soda.



It is evident from the (b) equations that one molecule of calcium bicarbonate requires one molecule of lime or two molecules of caustic soda, whilst double these quantities are necessary for the complete precipitation of one molecule of the magnesium compound. This latter fact is due to the solubility of normal magnesium carbonate, so that the precipitation is effected as hydrate.

It will be further noticed from an inspection of the second and fourth of the (b) equations that the use of sodium hydrate results in the formation of an equivalent amount of carbonate of sodium. This amount may actually be less than, just equal to, or greater than the amount required for precipitating the calcium salts of Class I. Accordingly there are three cases to be considered :

(1) When there is less sodium carbonate formed than is required for the precipitation of Class I. compounds, the softening of the water is accomplished by a mixture of caustic soda and carbonate of soda.

(2) When the sodium carbonate formed is just sufficient to precipitate Class I., sodium hydrate only is required.

(3) When the sodium carbonate formed is more than necessary, a portion of the caustic soda is replaced by lime, and the softening reagents will then be sodium and calcium hydrates.

The determination of the amounts of precipitants necessary will follow from the results of Kalmann's rapid analysis of the water, made as specified previously (page 249).

The method of calculation is appended :

Let  $x$  = amount of sod. carb. chemically equiv. to the cal. carb.

$y$ =	do.	do.	do.	mag. carb.
$z$ =	do.	do.	do.	other cal. salts.
$w$ =	do.	do.	do.	other mag. salts.

Then, having determined the combined carbon dioxide, let its sodium carbonate equivalent be called  $a$ . Thus

$$x + y = a \dots\dots\dots(1)$$

If  $b$  and  $c$  represent respectively the sodium carbonate equivalents of the total calcium and the total hardness

$$x + z = b \dots\dots\dots(2)$$

$$x + y + z + w = c \dots\dots\dots(3)$$

The sodium carbonate represented by  $z$  and  $w$  must be wholly or partly causticized, and from (1) and (3) this amount

$$z + w = c - a \dots\dots\dots(4)$$

Now, when sodium hydrate is used for precipitating the carbonates, it has been shown that an amount of sodium carbonate is formed equal to  $x + 2y$ . Of this amount  $z$  parts are required for the Class I. compounds, so that we have the three cases mentioned above according to whether  $x + 2y$  is less than, equal to, or greater than  $z$ , that is, according to whether  $x + 2y - z$  is negative, zero, or positive.

Now from (1) and (2)  $x + 2y - z = 2a - b$ .

We have therefore

(A)  $2a - b = -m$ . For softening, use  $m$  parts of sodium carbonate, and  $c - a - m$  parts of sodium hydrate.

(B)  $2a - b = 0$ . Use  $c - a$  parts of sodium hydrate.

(C)  $2a - b = +m$ . Use  $c - a$  parts of sodium hydrate and the equivalent in lime of  $m$  parts of sodium carbonate.

## CYLINDER DEPOSITS.

Cylinder deposits consist chiefly of organic matter formed by the decomposition of lubricants, but they may contain mineral matter which has been carried over from the boilers.

The most important determination in the analysis of a deposit is that of saponifiable oil. The oleic acid formed by saponification exerts a marked corrosive action on metals, and particularly on brasses. The action appears to consist in a dezincification, as the actual chemical analysis and microscopic examination of such corroded material show an excess of copper which has a spongy texture.

Mineral oils, consisting of hydrocarbons only, are almost universally used for lubrication, and they are not of course saponified by steam. Unfortunately, many samples of mineral oil contain appreciable quantities of animal oil, whilst, as they work considerably thinner when they become heated than animal oils, it is possible that the application of fat has been more than once resorted to by a tired engineer.

**Free Oils.**—A weighed sample of the deposit, previously dried, is exhausted with ether in a Soxhlet tube in the usual manner. The

solution contains the free oils, and evaporation of the ether yields their amount. To determine the separate amounts of animal and mineral oil a solution of alcoholic potash is added to effect saponification of the former, and after expulsion of the alcohol sufficient hot water added to dissolve the soap. The mineral oil is then removed, after cooling, by shaking with ether in a separating funnel and drawing off. Evaporation of the ether yields the mineral oil, which is then weighed. The soap solution is acidified with sulphuric acid, and the separated fatty acid collected as usual with a weighed piece of white wax.

The ethereal solution of the mineral oil may contain small quantities of such soaps as do not dissolve in water. The oil obtained should therefore be examined for lead, calcium, and zinc.

**Residue Insoluble in Ether.**—The examination of this is not important. Ignition at redness expels hydrocarbons insoluble in ether, together with free carbon, and the inorganic residue may be analyzed as usual.

Sometimes a deposit contains metallic iron, and ignition will oxidize some or all of this, whilst carbonates of calcium and magnesium will become oxides. An exhaustive analysis would thus involve a determination of free iron and of carbon dioxide.

TYPICAL ANALYSES.

Boiler Waters.			Boiler Scales.		
	I.	II.		I.	II.
Sodium Chloride, -	0·0091	0·0154	Siliceous matter, -	11·70	5·43
Sodium Sulphate, -	0·0009	0·0141	Ferric Oxide, Alumina, -	2·81	4·73
Potassium Sulphate, -	0·0027	0·0061	Calcium Sulphate, -	1·69	61·02
Calcium Sulphate, -	0·0321	nil.	Calcium Carbonate, -	5·45	20·81
Calcium Carbonate, -	0·0110	0·0833	Magnesium Carbonate, -	7·36	5·23
Magnesium Carbonate, -	0·0178	0·0338	Calcium Hydrate, -	13·70	—
Ferric Oxide, Alumina, -	0·0050	0·0020	Magnesium Hydrate, -	56·37	—
Silica, -	0·0082	0·0038	Moisture expelled at } 100° c., -	0·69	1·84
Organic etc., -	0·0177	0·0246	Undetermined and } Organic, -	0·20	0·71
	0·1045	0·1831		99·97	99·77
	grams per litre.	grams per litre.			
Analyst,	Stillman.	Stillman.	Analyst,	Stillman.	Authors.

## **PART X. THE ANALYSIS OF ENGINEERING ALLOYS.**

MORE pages are devoted to this subject than are usually considered necessary in books of this kind. We find, however, that these materials have to be dealt with in the steel-work's laboratory more or less frequently; we also find, particularly respecting white metal alloys, that simple means of estimating the main constituents without going through a maze of separations are not well known.

As far as possible our information and experience are presented so as to enable single elements, in either simple or complex alloys, to be determined without making preliminary separations, except merely incidental ones, as is commonly done in the analysis of iron compounds. That is to say, having found a suitable process, we have determined what elements do not interfere with it, and how to obviate the interferences of such as do. Provision may not thus have been made for every possible contingency, but we hope to have placed in the hands of analysts, who are also chemists, means whereby any of the innumerable industrial alloys of this class may be examined.

### **I. COPPER ALLOYS.**

#### **METALLIC COPPER.**

The various impurities of metallic copper can be determined with as great refinement as those of iron and steel, and perhaps even more successful efforts have been made to determine their state of combination. The following analysis of refined copper, by Hampe, illustrates this point:



Cu, -	-	-	-	-	-	-	-	-	-	99.1774
Cu <sub>2</sub> O, -	-	-	-	-	-	-	-	-	-	0.1662
Ag, -	-	-	-	-	-	-	-	-	-	0.0720
Au, -	-	-	-	-	-	-	-	-	-	0.0001
As, -	-	-	-	-	-	-	-	-	-	0.0476
As <sub>2</sub> O <sub>5</sub> , -	-	-	-	-	-	-	-	-	-	0.1273
Sb, -	-	-	-	-	-	-	-	-	-	0.0331
Sb <sub>2</sub> O <sub>5</sub> , -	-	-	-	-	-	-	-	-	-	0.0822
Bi <sub>2</sub> O <sub>3</sub> , -	-	-	-	-	-	-	-	-	-	0.0580
PbO, -	-	-	-	-	-	-	-	-	-	0.0650
Fe <sub>2</sub> O <sub>3</sub> , -	-	-	-	-	-	-	-	-	-	0.0900
Co, -	-	-	-	-	-	-	-	-	-	0.0113
CoO, -	-	-	-	-	-	-	-	-	-	0.0008
Ni, -	-	-	-	-	-	-	-	-	-	0.0631
NiO, -	-	-	-	-	-	-	-	-	-	0.0012
SO <sub>2</sub> , -	-	-	-	-	-	-	-	-	-	0.0020
										<hr/>
										99.9973

It need hardly be said that commercial analyses are not generally expressed with this elaboration.

The more important impurities are arsenic, antimony, bismuth, lead, iron, sulphur, and oxygen. Interesting accounts of the various modes of separating the preponderating copper from its impurities prior to a complete analysis will be found in the papers referred to under No. 1741 of the Bibliography. Instructions for the estimation of oxygen in copper of a varied and occasionally contradictory character may also be obtained from papers referred to under No. 1743.

#### Arsenic.

Dissolve five grams of the metal and a decigram of Swedish bar iron in nitric acid. Dilute to 200 c.c., neutralize most of the free acid with ammonia, and add an emulsion of magnesium oxide with a pipette to the boiling solution until it becomes dark olive green, and the iron is precipitated. An excess of magnesia should be avoided, as it increases the amount of copper carried down, and requires greater care to be exercised in the subsequent operations.

Allow the precipitate to settle, decant the solution through an asbestos filter, pour on the basic arsenate and antimonate of iron, and wash with hot water. The precipitate settles readily, and is more easily washed if magnesia is used to form it, than if alkalis or alkaline carbonates are used, but in any case it contains all the arsenic and antimony.

Make the filter as dry as possible by aspiration and split it. Use

the clean portion and a small plate to make a filter with *strong* hydrochloric acid. Stir up the remaining portion containing the precipitate with *strong* hydrochloric acid in a small beaker, pour into the filter just made, and wash with small portions of *strong* acid.

The solution is now treated like that of an iron ore on page 195, *i.e.* add a small excess of stannous chloride, saturate with sulphuretted hydrogen, collect the precipitated arsenious sulphide on the previously used asbestos filter, wash with strong hydrochloric acid saturated with sulphuretted hydrogen, and finally with water. The precipitate is then freed from traces of iron and copper, and the arsenic estimated with iodine, etc., as on page 105.

#### **Antimony.**

In order to estimate antimony on the same portion, it is desirable to have only very little copper associated with the basic ferric precipitate. To this end it may be necessary to re-dissolve in hydrochloric acid, and precipitate again as before.

Dilute the filtrate from the arsenious sulphide with five or six times its volume of hot water, and pass sulphuretted hydrogen. Collect the precipitated sulphides of copper and antimony on a hardened filter paper, wash back again into the flask, digest with a solution of sodium sulphide, remove the insoluble copper, and estimate antimony in the filtrate, after adding a few crystals of tartaric acid, exactly like arsenic. Fuller details of the titration are given on page 275.

#### **Arsenic and Antimony by Distillation.**

Both arsenic and antimony may be determined on one sample by a modification of the distillation process, which depends on the fact that the former is completely evolved at 115° C. and the latter not below 125° C. The considerable interval both in time and temperature affords ample opportunity of collecting both distillates separately and with certainty.

A solution which does not solidify at these elevated temperatures is obtained by adding 'Zinc Chloride' prepared as follows: saturate hydrochloric acid with metallic zinc, and evaporate until the liquid is of a viscous consistency, then mix with an equal volume of a solution of cupric chloride containing 100 grams of copper per litre. The mixture should be concentrated or diluted until it boils at 108° C. The following description of the operation is by Gibbs (*Journ. Soc. Chem. Ind.* 1901, 184).

The distillation is conveniently made in an ordinary 8 oz. round-bottomed flask, with a delivery tube fused into the neck. The neck is stoppered by a rubber bung, through which are inserted a thin thermometer registering to about  $250^{\circ}\text{C}$ , and so placed that the bulb reaches to within half an inch from the bottom of the flask, and a small separatory funnel, the tip of whose stem, reaching half way into the body of the flask, is drawn to a point and bent so as to carry the cold acid away from the thermometer. The end of the delivery tube is inserted through a bung in one arm of a three-bulb tube, standing in a trough of cold water, in which the distillate is condensed.

The basic ferric precipitate containing the arsenic and antimony which has been obtained in the above-described manner,<sup>1</sup> is placed in the flask with 50 c.c. of the 'zinc chloride' solution, and about quarter of a gram of the metallic sample; the latter acts as a reducing agent towards the arsenic and antimonious acids, and is itself dissolved by the cupric and ferric chloride in solution. The bung with the thermometer and funnel is replaced and the condensing tube containing just sufficient water to form a lute is connected.

The flask is heated through wire gauze, by a flame which just suffices to produce gentle ebullition, until the thermometer registers  $115^{\circ}\text{C}$ .; this requires about fifteen minutes from the time of first boiling. The condenser is then removed and a fresh one placed in position, but it is not necessary to meanwhile remove the burner or otherwise cool the flask, as all the arsenic has been volatilized and the antimony not yet begun to come off.

Having replaced the condenser the wire gauze is removed and the flask exposed to a strong naked flame so as to bring the temperature to  $150\text{--}160^{\circ}$  in from ten to fifteen minutes. About 10 c.c. hydrochloric acid are then run in from the separatory funnel. The entrance of the acid is so regulated that the dense white fumes formed produce a steady stream of gas from the flask, but liquid acid must not be allowed to fall on the fused zinc chloride. After adding hydrochloric acid the heating is continued until the flask is cleared of fumes; the temperature is then about  $200^{\circ}\text{C}$ . The condensing tube is then removed and both distillates titrated with iodine and starch in the usual manner.

The following interesting data were obtained from the distillation of a synthetic mixture containing 0.005 gram arsenic and 0.0015 gram antimony, by removing the distillates at intervals and titrating with

<sup>1</sup> Gibbs uses solid sodium bicarbonate instead of magnesia.

iodine solution, 1 c.c. of which was equal to 0·0005 gram arsenic or 0·0008 gram antimony.

	Temperature of Solution.	Iodine. c.c.
Boiled, - - - - -	108°	—
After 7 minutes, - - - - -	109°	4·2
After 12 minutes, - - - - -	110°	3·0
After 17 minutes, - - - - -	112°	2·8
After 22 minutes, - - - - -	115°	0·0
	Total,	10·0 =0·005 As.
After 5 minutes further heating,	118°	0·0
After 11 minutes further heating,	125°	0·2
After 13 minutes further heating,	160°	0·3
5 c.c. HCl was now added, a drop at a time, and heating continued for 7 minutes, - - - - -	195°	1·5
	Total,	2·0 =0·0016 Sb.

**Lead.**

Dissolve ten grams of copper in nitric acid, add 15-20 c.c. sulphuric acid, and evaporate until copious fumes of sulphuric anhydride have been evolved for about half an hour. In order to avoid the bumping which is apt to occur, the supernatant solution may be poured off and heated separately, but returned to the precipitated sulphate when each begins to fume.

Allow the beaker to cool, dilute to about 300 c.c., boil until the cupric sulphate is dissolved, and allow to stand all night. The possibly more correct practice of adding alcohol to decrease the solubility of lead sulphate is generally neglected in dealing with metallic copper, as the solubility of cupric sulphate is also much decreased. Collect the lead sulphate on a small pulp filter, wash once or twice with very dilute sulphuric acid, transfer precipitate, and filter, to a small beaker containing 10 c.c. strong ammonium acetate, heat and break up the filter, strain off the paper, and add 20 c.c. of an ammonium molybdate solution (4 grams molybdenum per litre) which has been made slightly acid with acetic. Collect the precipitated lead molybdate, ignite, and weigh.

Small amounts of lead may be precipitated as molybdate directly

from the cupric solution, but it requires a little practice to perform the operation satisfactorily.

Dissolve the sample as before, add ten grams of ammonium chloride and then ammonia until a precipitate just forms. Clear with hydrochloric acid, add 20 c.c. ammonium molybdate solution and 10 c.c. strong ammonium acetate and boil. Allow the cream-coloured precipitate to settle until the solution is nearly cold, or longer, then filter off and wash with water containing a little ammonium acetate and a few drops of the ammonium molybdate solution. Re-dissolve the precipitate in hydrochloric acid, repeat the above operations to eliminate a small amount of copper which has been precipitated, and weigh finally as lead molybdate. The results are somewhat higher than those obtained by the former process.

#### Bismuth.

According to Stone (*Journ. Soc. Chem. Ind.* 1887, 416), as little as one-tenth of a milligram of bismuth in ten grams of metallic copper can be detected in the following manner.

Dissolve in nitric acid, add an excess of a mixture of ammonia and ammonium carbonate, filter, and wash with a dilute solution of the precipitant. Dissolve the precipitate in a small quantity of dilute sulphuric acid, add a crystal of potassium iodide and afterwards a small excess of sulphurous acid to remove the colour produced by the iodine liberated by any iron present. The persistent bright yellow colour due to bismuth may be matched by adding a standard solution of bismuth sulphate to acidified water containing a crystal of potassium iodide.

We have regularly used this iodide reaction for estimating small amounts of bismuth in white metal alloys as well as in copper. As it has been condemned on account of its supposed subjection to numerous interferences, the following tests may be worthily recorded:

A standard bismuth solution was prepared by dissolving 1.114 grams of the sesqui-oxide in hydrochloric acid (or one gram of the metal in nitric acid), evaporating to fumes with 20-25 c.c. sulphuric acid, and diluting to a litre. A standard colour was prepared by mixing 4 c.c. of this solution with 2 c.c. dilute sulphuric acid (1 to 3), 5 c.c. of a five per cent. potassium iodide solution and water to 70 c.c. This colour was compared with that formed under the following varying circumstances:

**Sulphuric Acid.**—Increasing excesses of acid darken the colour slightly, but several times as much as was in the standard introduced no appreciable error.

**Nitric Acid.**—As sulphuric acid. When enough acid is present to decompose the potassium iodide and liberate a little iodine, a few drops of sulphurous acid should also be added.

**Hydrochloric Acid** bleaches the colour considerably; the effect is less the more sulphuric acid or potassium iodide the solution contains, but its presence, and that of alkaline chlorides, should be avoided.

**Acetic Acid.**—As sulphuric acid.

**Sulphurous Acid.**—The colour is only slightly darkened by very large amounts. Of other reducing agents: thiosulphate bleaches the colour, but less readily the more iodide or sulphuric acid there is present; stannous chloride bleaches the colour only by virtue of the hydrochloric acid it contains.

**Alkaline Salts.**—Ammonium nitrate or sulphate do not interfere more than their acids. Ammonium acetate destroys the colour completely if sufficient is added to neutralize all free mineral acid.

**Potassium Iodide.**—The first drop produces no colour; the maximum colour is reached when between two and three c.c. are added; any excess beyond this is without effect.

**Temperature.**—The colour is a shade lighter at 100° C. When 25 per cent. of the liquid was boiled away and replaced by distilled water, the colour was hardly affected.

A decigram of each of the following metals was added to their respective solutions.

**Iron.**—Free iodine liberated by the ferric salt. After removing with a small excess of sulphurous acid, the colour was equal to that produced by 4.4 c.c. standard bismuth sulphate instead of 4.0 c.c.

**Copper.**—The operation cannot be performed in sulphuric acid solutions, as both metals are precipitated as a dark brown compound. Perfect results are obtained by proceeding as follows: Add an excess of ammonia, then an excess of acetic acid, and more than enough potassium iodide to precipitate the copper; destroy the free iodine with an excess of sulphurous acid, dilute, and filter. Add sulphuric acid to the nearly colourless filtrate and compare the re-formed colour with the standard. As little as 0.01 per cent. bismuth in metallic copper can be readily estimated by dissolving half a gram in nitric acid and proceeding as above.

**Lead.**—The colour is darker when very small amounts of lead are present. The solution should be evaporated with sulphuric acid, then filtered after adding potassium iodide and the colour of the filtrate

compared. If much lead is in solution it is precipitated on adding the iodide as a deep reddish-brown compound containing bismuth: this is the characteristic feature of Abel and Field's test for bismuth in copper.<sup>1</sup>

**Tin.**—The mixed solutions were boiled with nitric acid, potassium iodide added, and the filtrate compared: result accurate.

**Antimony.**—Results accurate when treated like tin. If the mixture is evaporated with sulphuric acid, to eliminate chlorides for example, the results are much too low, and entirely worthless.

**Arsenic.**—If the free iodine liberated by arsenates is destroyed by sulphurous acid, the results are accurate.

**Silver.**—Destroy free acid with ammonium acetate, add an excess of iodide, and filter off the pale yellow silver iodide. Acidify the filtrate and compare: the results are accurate.

**Zinc, Manganese, and Aluminium.**—These metals do not interfere in any way.

#### Sulphur.

Dissolve ten grams of the sample in nitric acid, evaporate to dryness, re-dissolve in hydrochloric acid, re-evaporate so as to eliminate nitric acid, and again re-dissolve. Evaporate the acid solution to low bulk, dilute, and filter off any insoluble residue. The residue is fused, extracted with water, and filtered. The two filtrates are mixed, precipitated with barium chloride, and the estimation finished as though a steel were being dealt with.

#### Iron.

Dissolve five grams in nitric acid, dilute to 500-600 c.c., add five grams of ammonium chloride and an excess of ammonia. Boil, filter,

<sup>1</sup> This test is made as follows: "About six grams of the copper to be examined are dissolved in nitric acid, a solution of lead nitrate, equal to three or four decigrams of the salt, is added, and then ammonia and ammonium carbonate. The precipitate is washed with ammoniacal water and dissolved in warm acetic acid. Considerable excess of potassium iodide is introduced, and the liquid is warmed until the precipitate disappears. On cooling, the crystalline scales will show by their colour the presence or absence of bismuth. If the least trace of bismuth is present the precipitated scales are no longer yellow, but assume a dark orange or crimson tint varying in intensity of colour according to the amount of bismuth present; a fiftieth part of a milligram can be easily detected." A modified form of this process is mentioned by Watson (*Journ. Soc. Chem. Ind.* 1887, 416).

and wash with faintly ammoniacal water. Then re-dissolve and re-precipitate, and estimate the ferric hydrate volumetrically or colorimetrically, in the usual way, according to its amount.

### Copper.

The following process depends on the precipitation of copper as sub-iodide and titration of the liberated iodine with thiosulphate and a starch indicator. It is perhaps the most satisfactory process known for the estimation of both large and small amounts of copper. The appended description is of a general nature, and is not intended to apply merely to the assay of the crude or refined metal.

The acid solution containing copper is made faintly alkaline with ammonia or sodium carbonate, and then distinctly acid with acetic; two or three grams of potassium iodide are added, and the mixture allowed to stand a minute or two. A decinormal solution of thiosulphate is run in from a burette until the colour of free iodine is barely distinguishable, and then 2 c.c. of freshly prepared starch liquor, and more thiosulphate drop by drop until the blue colour disappears. The change is usually quite sharp, but in impure solutions a purple or reddish colour may momentarily intervene between the distinct blue and the cream colour of the precipitated cuprous iodide. The end point, according to Garrigues, is sharper in sulphuric acid than in acetic acid solutions; this advantage, however, is more than counterbalanced by the interference exerted by arsenic and bismuth in the former case. The thiosulphate is best standardized with metallic copper of known purity, or with a quite definite and pure copper salt.

The results of the following tests made some years ago are in agreement with those obtained by others, and have been abundantly confirmed during the assay of various commercial compounds. Each test was made on a solution containing 0.14 grams of copper and a decigram of the foreign element. In the presence of salts of calcium, barium, strontium, magnesium, zinc, cadmium, arsenic, molybdenum, nickel, cobalt, uranium, and manganese, the amount of thiosulphate did not vary more than 0.05 c.c. from 22.4 c.c., and the course of the operation was perfectly normal.

**Lead.**—22.4 c.c. thiosulphate were required. Although lead iodide was formed the end reaction was quite distinct. The interference may be altogether avoided by adding sulphuric acid before neutralizing.

**Mercury.**—22.5 c.c. required: the mercuric iodide formed did not seriously interfere with the end reaction.



**Silver.**—22·4 c.c. required: the colour of the silver iodide as with lead and mercury prevents the disappearance of the free iodine colour being taken advantage of, but the starch-blue end-reaction is sharp.

**Aluminium.**—22·4 c.c. required: this metal is commonly used to deposit copper from a solution containing other metals prior to a cyanometric or iodometric estimation.

**Tungsten.**—22·3 c.c. required: the blue colour recurred slightly.

**Bismuth.**—22·5 c.c. required: a little sodium acetate should be present. See estimation of bismuth in the presence of copper, page 262.

**Tin.**—22·3 c.c. required: the excess of acetic acid did not clear up the precipitate after sodium carbonate had been added.

**Iron.**—(25 +  $x$ ) c.c.: the starch colour recurs. After adding sodium phosphate there was a persistent starch colour up to 20 c.c., it then recurred with decreasing rapidity up to 22·0 c.c.; after that it did not recur for fifteen minutes.

**Alkaline Salts.**—Ten grams of either the chloride, nitrate, or sulphate of ammonia, or the chloride or nitrate of sodium or potassium are without appreciable influence.

But the *acetates* of both sodium and ammonium prevent the complete precipitation of cuprous iodide. An excess of 50 c.c. acetic acid of B.P. strength is without influence, so that by adding a mineral acid (hydrochloric) short of excess the reaction proceeded as usual, and 22·45 and 22·50 c.c. thiosulphate were required.

In the presence of sodium sulphate the result was high and the starch colour recurred.

**Potassium Iodide.**—An excess is without influence. According to the equation



about five and a quarter grams of iodide are actually used for each gram of copper. Twice this amount is generally considered to be a safe working excess.

**Temperature.**—

Temperature,	25°	40°	50°	70° C.
Thiosulphate,	22·45	22·4	22·45	22·2 c.c.

At 70° C. iodine fumes were visible above the solution.

**Volume of Solution.**—

Volume,	-	-	100	200	400 c.c.
Hypo,	-	-	22·45	22·40	22·45

The colour disappeared when 20 c.c. thiosulphate had been added to

the last solution ; it recurred every half minute or so up to 22·2 c.c., and then more slowly up to 22·45 c.c.

**Amount of Copper.**—I. Milligrams copper present ; II. Volume of thiosulphate required ; III. Calculated volume of thiosulphate, taking the largest amount of copper used as standard.

I.	4	8	20	60	100	140	200	400
II.	0·60	1·25	3·05	9·2	15·25	21·40	30·35	60·70
III.	0·60	1·20	3·04	9·1	15·17	21·25	30·35	—

The volume of solution in each case was 200 c.c. ; with the smaller amounts of copper the starch blue recurred, but there was no doubt about the real end reaction.

COPPER-ZINC ALLOYS.

*Brass*<sup>1</sup> which is the most important of these alloys, contains roughly two-thirds copper and one-third zinc, and more or less of the impurities commonly associated with these metals. *Muntz metal*, *Pinchbeck*, and *Mannheim gold* are examples of other copper-zinc alloys which differ in the proportion of constituents according to their intended uses. *Sterro*, *Aichs'*, and *Delta metal* contain from one to four per cent. of iron and sometimes also small amounts of phosphorus.

Copper, iron, lead, arsenic, antimony,<sup>1</sup> and bismuth may be estimated separately as in metallic copper. A number of constituents may be estimated on one sample as follows :

Dissolve two grams of the alloy in nitric acid, evaporate to low bulk, and filter. If the residue is very small it is ignited and weighed as stannic oxide ; otherwise it must be examined as on page 268.

Add 10 c.c. sulphuric acid to the filtrate and evaporate to fumes, dilute to about 150 c.c., collect the lead sulphate, transform it to molybdate as on page 260, ignite, and weigh.<sup>2</sup>

Dilute the filtrate to 200 c.c., measure out 50 c.c. (half a gram of the alloy), and estimate copper by the previously-described iodide process.

Warm the remaining 150 c.c. of solution and add excesses of sulphurous acid and ammonium (not potassium) thiocyanate to precipitate the copper. Allow the solution to stand until cleared, then filter and wash, or if preferred, filter off a suitable fraction. The filtrate

<sup>1</sup> The presence of antimony causes brass to crack on the edges during rolling.

<sup>2</sup> Lead up to two per cent. is purposely added to brass which has to be machined in order that the turnings may break short and thus prevent the tool from becoming clogged.

may then be boiled, to get rid of sulphurous acid, saturated with sulphuretted hydrogen, any precipitated arsenic, antimony, bismuth, etc., removed, the solution again boiled to eliminate sulphuretted hydrogen, oxidized with nitric acid, saturated with ammonia, and any small amount of iron collected. But if these elements are not present in appreciable amounts the estimation of zinc may be proceeded with according to the following instructions without troubling to remove the excess of thiocyanate.

### Zinc.

Zinc is most accurately determined as the double ammonium-phosphate, or as pyro-phosphate. Fixed alkalis, especially potassium, should not be present, nor should salts of manganese, iron, copper, nickel, or cobalt.

The process was originally proposed by Guyard (*Chem. News*, xxiv. 148), and has been studied by Lösekan and Meyer (*Chem. Zeit.* 1886, 729 and 1605, and *Chem. News*, lvi. 68), Clark (*Journ. Soc. Chem. Ind.* 1896, 867), Garrigues (*Jour. Amer. Chem. Soc.* xix. and *Chem. News*, lxxvii. 41), Austin (*Amer. Jour. Scien.* viii. and *Chem. News*, lxxx. 305), Dakin (*Zeit. f. Anal. Chemie*, xxxix. 373, and *Chem. News*, lxxxii. 101), Walker (*Jour. Amer. Chem. Soc.* xxiii. and *Chem. News*, lxxxv. 18), and others. Where accurate work has to be done it is worth while practising the method on synthetic solutions, so as to realize the best working conditions. The operations are performed as follows:

The acid solution of zinc, which should contain several grams of ammonium chloride, is neutralized or made faintly alkaline, and then made faintly acid; methyl-orange, or a piece of litmus paper floated in the liquid being used as indicator. The solution is then heated nearly to boiling, and from ten to twenty times as much ammonium phosphate or microcosmic salt added as there is zinc present. The solution, which is now alkaline to red litmus paper, is kept heated until the amorphous flocks of zinc phosphate become transformed to the dense crystalline zinc ammonium phosphate. It is then allowed to settle, filtered, the beaker cleaned with the mother liquor, and the precipitate washed with hot water.

The precipitate may be dried at 100° C., and weighed as zinc ammonium phosphate, which contains 36.49 per cent. zinc; or it may be ignited and weighed as pyrophosphate, which contains 42.55 per cent. zinc. The ignition can be made without fear of any zinc being volatilized, though the separate ignition of precipitate and paper is considered necessary. We have, however, with satisfaction, collected

the precipitate on pulp filters, ignited gently at the mouth of the muffle in porcelain crucibles, and then more strongly to perfect whiteness, and either weighed in the crucible or brushed out. We have also filtered through asbestos in the following way :

Pierce the bottom of a porcelain crucible from the outside by a smart stroke with a sharp file tang, and widen the hole to quarter of an inch or so. Rest a filter plate in the crucible and cover it with asbestos fibre in the usual way. Support the crucible in a funnel on a hollow rubber ring, and arrange the apparatus for filtration by suction. After washing the crucible is removed to a platinum dish, ignited, and weighed. The precipitate is then dissolved in hot dilute hydrochloric acid, washed, and the crucible and felt again weighed. The same asbestos felt serves over and over again without re-arranging. The ignition to pyrophosphate is complete at low redness; if heated *very strongly* it melts, and is absorbed by the asbestos, but does not lose weight to any appreciable extent : thus 1.173 grams pyrophosphate lost only 1.3 milligrams :

The following results show that either procedure is reliable :

Zinc Present.	Zinc found using	
	Paper Pulp.	Asbestos.
0.0498	0.0499	—
0.0995	0.0993	0.0999
0.1493	0.1490	0.1494
0.2488	0.2496	—
0.2985	0.2991	0.2995
0.4975	0.4973	0.4980

### COPPER-TIN ALLOYS.

Dissolve one or two grams of the bronze in strong nitric acid, evaporate just to dryness, add 40-50 c.c. five per cent. nitric acid, boil, and filter. Ignite in a porcelain crucible, and weigh the residue: it consists of stannic oxide, and more or less of the oxides of copper and lead, besides practically all the antimony, arsenic, iron, and phosphorus, if these are present in small amounts compared with the tin. The addition of ammonium nitrate to the acid liquor is said to avoid the formation of basic copper salts, but as it sometimes unexpectedly leads to other troubles, it is better to proceed as follows :

Mix the ignited residue with about ten times its weight of sodium

thiosulphate and fuse. Extract the fusion with water, collect the precipitated sulphides of copper, lead, and iron, and subtract their weight after ignition from the former weight of the impure stannic oxide. The difference is roughly the weight of oxide corresponding to the tin in the alloy. The result is only approximate, because the lead and iron are not weighed in each case as identical compounds, and because the sulphide of copper may be partly dissolved by the sodium sulpho-stannate, as is explained on page 281. Any arsenic, antimony, and phosphorus also pass into solution and are reckoned as tin. An actual estimation of the tin is made by acidifying the filtrate, reducing it with metallic antimony or iron, and titrating with decinormal iodine, as in the analysis of white metal alloys.

The small amounts of copper, lead, and iron separated from the tin are dissolved in hydrochloric acid and returned to the main filtrate, which is then evaporated with sulphuric acid. The precipitated lead sulphate is collected and transformed to molybdate as before (page 260).

The copper is then removed with sulphurous acid and ammonium thiocyanate, and the zinc and iron estimated in the filtrate as in the analysis of brass.

A separate portion is dissolved in aqua regia for the iodometric estimation of the copper. Or one of the modes of assaying the precipitated cuprous thiocyanate mentioned in the Bibliography may be employed.

### ALLOYS CONTAINING PHOSPHORUS.

Alloys of copper and tin in varying proportions containing small amounts of phosphorus up to two per cent., are known as phosphor-bronze. One or two tenths per cent. phosphorus may also be found in some copper-zinc alloys, such as Delta metal.

Three methods are in common use for estimating the phosphorus, apart from those involving volatilization in a stream of chlorine or electrolytic depositions. They are :

- (1) Decompose the bronze with nitric acid, evaporate to low bulk, dissolve the precipitated metastannic acid in hydrochloric acid, saturate the diluted solution with sulphuretted hydrogen, evaporate the filtrate with nitric acid and precipitate phosphorus with nitro-molybdate solution (Fresenius). Hempel objects to this process, because some phosphorus is invariably carried down by the sulphide of tin.

- (2) Add excess of ammonia to an aqua-regia solution of the alloy, pass sulphuretted hydrogen, remove sulphides of copper, lead, etc., add ammonia and magnesia mixture to the filtrate, and ignite the precipitate to magnesium pyrophosphate as usual (Wickhorst).
- (3) The stannic oxide obtained from the nitric acid solution of the alloy is washed, dried, and ignited in a porcelain crucible, and then fused with three or four times its weight of potassium cyanide at a red heat. The melt is then extracted with water, metallic tin removed, hydrochloric acid added, cyanogen compounds boiled off, the solution evaporated to small bulk, and the phosphorus precipitated with magnesia mixture (Oettel).

We prefer the last method, but add ferric chloride after boiling off cyanogen compounds, and then precipitate a basic ferric phosphate with ammonia, dissolve it in nitric acid, and estimate the phosphorus *via* phospho-molybdate and lead molybdate.

### ALLOYS CONTAINING MANGANESE

Manganese—*i.e.* spiegeleisen or ferro-manganese—is added to copper, with tin and zinc in varying proportions, in order to render the alloy more homogeneous, harder, and stronger. These alloys are all spoken of as manganese bronze, although the manganese may vary from two-tenths to nearly twenty per cent. We have analyzed and collected analyses of manganese bronzes from various sources. The enormous variation in their composition—and in the composition of engineering alloys generally, which pass under a common name—requires the analysis of each sample to be made independently; that is to say, no set process can be adhered to.

The manganese can be separately and accurately estimated by the bismuthate process, exactly as in steel. The chlorate process has also been successfully used.

### COPPER-ALUMINIUM ALLOYS.

The alloys of this class are 'aluminium bronze,' which consists for the most part of aluminium and copper; 'aluminium brass,' which contains in addition a considerable quantity of zinc, and combinations of aluminium and copper with some other metal or metals. The alloy of

ninety parts copper and ten parts aluminium, which is a definite chemical compound, was discovered by Dr. Percy.

According to Regelsberger, the most useful aluminium bronzes contain from five to twelve per cent. aluminium; if more than twelve per cent. be present the alloy is brittle and unworkable. Silicon is often purposely added, as it increases the tensile strength: the maximum is two and a half per cent. An alloy containing three per cent. aluminium has almost the colour of copper; with three to four per cent. it has the colour of a reddish sample of gold; with five per cent. the colour is golden yellow, and with increasing amounts the alloy becomes yellowed until with fifteen per cent. aluminium the colour is nearly white, with a reddish tinge. 'Aluminium brass' contains up to three and a half per cent. aluminium.

**The Analysis of Aluminium Bronze** is very simple. For the estimation of silicon two or three grams of the alloy are dissolved in aqua regia, the solution evaporated with sulphuric acid, and the silica collected and weighed in the usual manner. Subsequent treatment with hydrofluoric and sulphuric acids should not be omitted, as the residue may also contain small amounts of lead sulphate or stannic oxide.

The copper and aluminium are separated in the sulphuric acid solution by means of sulphuretted hydrogen, thiosulphate, or ammonium thiocyanate, as already described, and the former estimated iodometrically from the precipitate, or on a separate sample. The aluminium in the filtrate is precipitated and estimated as phosphate.

**The Analysis of Aluminium Brass** differs from the above only in requiring zinc and aluminium to be separated. This is accomplished as follows:

To the warm solutions of the two metals add rather more of a solution of sodium cyanide than is needed to form a double cyanide  $[\text{Zn}(\text{CN})_2 \cdot 2\text{NaCN}]$  with the zinc. Then add a few grams of ammonium chloride if such is not already present, and make faintly but distinctly alkaline with ammonia. The solution may, but need not, be heated to boiling. A fraction of the solution is filtered off, acidified, and boiled to remove cyanogen compounds, and then neutralized, made faintly acid, and the zinc precipitated and estimated as phosphate.

The aluminous residue and filter, from which the liquid is allowed to drain, is heated with dilute hydrochloric acid, the paper strained off, sodium phosphate added, the acidity adjusted, acetic acid equal to from five to ten per cent. the volume of the solution added, then thiosulphate, and the estimation as aluminium phosphate completed in the usual manner.

If sodium cyanide is not at hand the purest obtainable potassium cyanide may be used, but the zinc pyrophosphate will then be contaminated with potash salts to the extent of about one per cent., and it will fuse more readily. The value of the cyanide solution is determined by titrating it against a known amount of nickel. As much may then be added to the solution of zinc and aluminium as would be required if the former metal were nickel.

TYPICAL ANALYSES.

	Brass.	Delta Metal.	Naval Bronze.	Phosphor Bronze.	Aluminium Bronze.	Manganese Bronzes.	
Copper, - -	65.52	60.00	88.10	86.12	88.40	61.60	82.11
Zinc, - -	32.21	35.66	2.04	—	—	35.77	0.81
Tin, - -	0.35	1.74	9.74	9.24	—	0.75	1.50
Lead, - -	1.80	1.41	—	3.43	—	—	—
Aluminium, -	—	—	—	—	9.14	0.38	0.20
Manganese, -	—	—	—	—	—	0.28	14.22
Iron, - -	0.03	0.76	0.09	—	0.21	1.00	1.28
Phosphorus, -	—	0.16	—	0.51	—	—	—
Silicon, - -	—	—	—	—	1.73	—	—
	99.91	99.73	99.97	99.30	99.48	99.78	100.12

II. WHITE METAL ALLOYS.

The preponderating constituents of such white metal anti-friction alloys as are considered here are Tin, Lead, and Antimony, with smaller amounts of copper, and still smaller amounts of iron, bismuth, and arsenic. White anti-friction alloys containing large amounts of zinc may be analyzed by methods given in the preceding section.

We propose to consider the estimation of the preponderating elements singly, and then to describe a process for the general analysis.

ESTIMATION OF TIN.

In Pure Solutions :

A hydrochloric acid solution of stannous chloride can be very accurately titrated with iodine, using the starch indicator.

The reduction of stannic to stannous chloride is generally accomplished with metallic iron. It is quicker, however, to use pure metallic anti-



mony which has been ground in an agate mortar until the particles no longer glisten. A small excess of this material will reduce a solution completely by one minute's boiling, and as it exerts no influence during the subsequent titration of the cold solution the excess need not be removed. In fact its presence may be advantageous, as during cooling any accidental re-oxidation while the solution was still hot would be corrected. As the solution cools the antimony is less able to correct such a mishap.

A determination is made as follows: Heat the solution containing about one-fifth its volume of hydrochloric acid, add a small amount of powdered antimony, and boil. The reduction is conveniently made in such an arrangement as is shown in figure 10 (page 108), and the solution is cooled out of contact with air by dipping the tip of the bent tube into an emulsion of sodium bicarbonate made with freshly-boiled water. Two c.c. starch solution are then added, and decinormal iodine run in from a burette until a permanent blue colour is formed.

$$1 \text{ c.c. } \frac{N}{10} \text{ iodine} = 0.0059 \text{ gram tin.}$$

If stannous chloride solutions need diluting it is *essential* that water free from dissolved oxygen should be used. Beringer secures water in such a state by adding a gram of sodium bicarbonate, and 2 c.c. hydrochloric acid to each 100 c.c. of water: the effervescence sweeps out the dissolved oxygen.

It may sometimes be desired to repeat the estimation in the same liquid by again boiling, cooling, and re-titrating. This, however, cannot be done satisfactorily with metallic antimony as reducing agent. With iron as reducing agent one and the same solution may be re-assayed as often as is desired.

*Proportion of Tin.*

Added, - -	·1750	·1000	·0480	·0200	·0080 grams.
$\frac{N}{10}$ Iodine, -	29.7	16.9	8.3	3.4	1.4 c.c.
Found, - -	·1752	·0997	·0490	·0201	·0083 grams.

*Hydrochloric Acid.*—Experiments in which the proportion of acid of 1.16 specific gravity varied from one tenth to one half the volume (150 c.c.) of solution gave results varying from 99.5 to 101 per cent.

**In the Presence of Other Elements.**

*Iron.*—Exercises no influence. When metallic iron is used to reduce the tin, and antimony chloride is also present, the appearance of metallic antimony is an indication that the tin is completely reduced.

Much less iron may be used than is usual, and with greater certainty, by taking advantage of this fact.

*Chromium and Nickel.*—Exert no interference other than may be due to the colour of their chloride solutions, and that is not serious.

*Zinc, Manganese, and Aluminium.*—Do not at all interfere.

*Copper.*—Is reduced to cuprous chloride. If the iodine is added in brisk drops to the vigorously agitated solution, so that no local excesses of iodine are formed, the results are accurate. But the results are seriously out when local excesses of iodine are allowed; *e.g.* only 0.1239 gm. tin was registered instead of 0.1500 when 20 c.c. N/10 iodine was run into the solution containing 0.05 gm. copper, without shaking, and then finished as usual. A white precipitate (cuprous iodide) forms. In order to delay the formation of this precipitate, and also to assist the precaution just named, it is advisable to have larger amounts of hydrochloric acid present; say, one-third the volume of acid of 1.16 specific gravity.

*Cobalt.*—The results were a little high, but so little that one hesitates to say that cobalt exerts any influence; *e.g.* 0.1510 gm. tin instead of 0.1500.

*Lead.*—Without influence. In very dilute acid solutions lead iodide may form; but, by titrating in very acid solutions so as to prevent this, there is no difficulty when three or four times as much lead as tin is present.

*Bismuth.*—The yellow colour which bismuth forms in potassium iodide solutions does not interfere much with the starch blue. There is no other interference.

*Phosphorus and Sulphur.*—Sodium phosphate and sulphate added to the stannic chloride exerted no influence.

*Mercury.*—Is reduced to the metallic state. In hot solutions finely-divided mercury exerts a limited reducing action on stannic chloride; it is inert in cold solutions.

*Molybdenum.*—The characteristic  $\text{Mo}_2\text{O}_3$  colour forms when the solution is but moderately warm, but it is not appreciably re-oxidized by the iodine. The starch-blue is very slowly discharged; this, however, leaves no uncertainty in the mind, because the normal end-reaction is so very sharp and decisive.

*Tungsten.*—Lower oxides are also formed. The solution may be light blue, but the starch (dark) blue can be readily distinguished notwithstanding.

*Arsenic.*—This element interferes very seriously if more than one part to two hundred parts of tin is present. A black graphitic looking

precipitate (arsenide of tin) insoluble in dilute hydrochloric acid is formed. Equal portions of a solution of stannic chloride were reduced and titrated in the presence of small amounts of arsenic with the following results:

Milligrams Arsenic present, -	-	3.75	1.875	0.75	0.00
c.c. $\frac{N}{10}$ Iodine required, -	-	16.5	21.2	25.5	25.8

### Direct Estimation of Tin in Alloys.

Dissolve one gram of the alloy in the form of thin shavings with hydrochloric acid and potassium chlorate, as is more fully described in the general analysis on page 280. Dilute to 100 c.c., measure out as much of the solution as contains about 0.15 gram tin, dilute to about 150 c.c. with water containing one-fifth its volume of hydrochloric acid, reduce with antimony, and titrate with iodine.

If the alloy contains appreciable amounts of arsenic the strong acid solution is treated with sulphuretted hydrogen as described on page 280; but instead of adding stannous chloride a small piece of the alloy weighed off is reserved and used to destroy traces of free chlorine and effect the reduction of the arsenic. The piece used should be hammered *very* thin and be hardly bigger than is just necessary to destroy the colour of the solution. A few drops of a solution of stannous chloride may be used instead, but its equivalent amount of tin must be finally deducted. The filtrate from the arsenious sulphide is diluted until the tin begins to precipitate, and then the sulphuretted hydrogen boiled off or destroyed with a crystal of potassium chlorate. The tin is then reduced with antimony and estimated as before.

### ESTIMATION OF ANTIMONY.

#### In Pure Solutions.

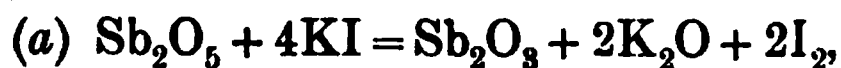
Mohr's process for the estimation of antimonious oxide is both convenient and exact. It depends on the reaction



which takes place in a solution containing an excess of alkaline bicarbonate.

The reduction of antimonious to antimonious oxide can be made in distinctly acid solutions with sulphur dioxide. It is advisable to add a crystal or two of potassium iodide, as it helps the reduction; in fact it may be completed with this assistance in such faintly acid solutions as

sulphur dioxide alone will scarcely affect. As very much less than the theoretical amount of iodide is needed the reduction may be supposed to occur in two stages :



i.e. the potassium iodide acts simply as a catalytic agent.

Antimonic oxide in an acid solution is determined by adding a crystal of potassium iodide and an excess of sulphurous acid. The solution is boiled until sulphur dioxide is completely driven off, a little tartaric acid is then added, the solution cooled, nearly neutralized with ammonia or sodium hydrate as in the estimation of arsenic (page 105), and an excess of 20 c.c. saturated sodium bicarbonate solution added, and then decinormal iodine until a permanent starch blue forms.

$$1 \text{ c.c. } \frac{\text{N}}{10} \text{ iodine} = 0.0060 \text{ gram antimony.}$$

*Effect of Varying Antimony.*

Milligrams Sb,	-	19	38	76	152	190
c.c. Iodine,	-	3.15	6.35	12.70	25.40	31.75.

**In the Presence of Other Elements.**

If a solution already contains antimonious oxide the addition of an equal amount of either magnesium, aluminium, zinc, lead, tin, copper, nickel, silver, iron, arsenic<sup>(v)</sup>, uranium, or the alkaline earths causes no interference. Mercuric salts do. The titration also may be performed at any temperature up to 60° C., and in solutions at any practicable dilution without inconvenience.

When a solution of antimonic oxide was reduced in the above-described manner with potassium iodide and sulphur dioxide the observed interferences were as follows. Each test solution contained 0.12 gram antimony and a decigram of the foreign element.

*Zinc.*—Found 0.1200 gram. Extra tartaric acid should be added to keep zinc in solution.

*Tin.*—Found 0.1996 gram. Tin is precipitated by sulphur dioxide unless the solution is freely acid. Extra tartaric acid should also be used or tin is precipitated by the bicarbonate and encloses some antimony: this makes the result low or causes a recurring end reaction. In any case when a precipitate forms the reaction is materially assisted by heating the solution to about 40° C.

*Nickel, Cobalt, Uranium, Chromium, Lead, Aluminium, and Manganese.*—These metals are entirely without influence, except the very slight one due to coloured solutions, providing also enough tartaric acid

is added to 'keep up' metals which would otherwise be precipitated. The amounts of antimony found varied between 0.1195 and 0.1200.

*Iron.*—Interferes greatly. 0.1590 gram antimony registered. The separation of antimony and iron is easily accomplished by precipitating the former with sulphuretted hydrogen.

*Copper.*—The interference of this metal is very erratic, but it can be easily got rid of by adding sulphurous acid and more potassium iodide than is needed to completely precipitate it. The hot solution is then filtered to remove cuprous iodide, boiled until free from sulphur dioxide and titrated as usual. Results were 0.1194 and 0.1200 gram antimony.

#### Direct Estimation of Antimony in Alloys.

Dissolve the alloy with hydrochloric acid and potassium chlorate, make the solution up to a definite volume, add a liberal excess of tartaric acid to a suitable fraction of it, and make the titration with such modification as may be imposed by the presence of copper, etc.

Any arsenic in the alloy would be estimated as antimony, supposing the decomposition were made so as to avoid loss by volatilization. It may be separately estimated and allowed for, or the antimony may be estimated on the filtrate after removing arsenious sulphide, as in the case of tin (page 275).

When an alloy contains very little antimony and much tin, a partial separation may be made by diluting the filtrate from the arsenious sulphide until a very decided precipitate is formed. This precipitate will contain all the antimony and a greater or less portion of the tin, according to the degree of dilution. Loviton (*Jour. Soc. Chem. Ind.* 1888, 403) maintains that a perfect separation of antimony from tin can be made by passing sulphuretted hydrogen into suitably acidified solutions.

#### ESTIMATION OF LEAD.

##### In Pure Solutions.

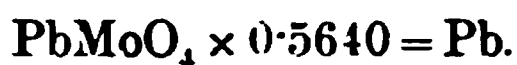
The fact that lead molybdate is exceptionably insoluble in solutions from which it may be precipitated, and that the ratio  $\text{Pb} : \text{PbMoO}_4$  is lower than the corresponding ratio for either sulphate or chromate, and that the precipitate may be safely ignited along with the paper, are reasons for preferring the following to the methods by which lead is generally estimated :

Chatard says,<sup>1</sup> "I tried to determine lead as molybdate, but without

<sup>1</sup> *Chemical News*, xxiv. 175.

success, as the presence of an excess of the precipitant seems to exert an injurious effect, the filtrate or washings speedily becoming cloudy." In quite pure solutions the precipitate has a colloidal form, but it at once flocks out if ammonium chloride is added, and may then be filtered and washed with ease. The operation is performed as follows:

Make the solution slightly ammoniacal, and then distinctly acid with acetic, add several grams ammonium chloride and heat the solution to boiling. Now add an excess of ammonium molybdate to the agitated liquid, boil a minute or two, allow to settle, filter through pulp, wash with hot water, ignite, and weigh.



#### **In the Presence of Other Elements.**

The above simple form of the process gives good results in the presence of a number of elements, but is greatly interfered with by others. It is not nearly so satisfactory in this respect as the converse estimation of molybdenum as lead molybdate even when the 'acid precipitation' subsequently referred to is adopted.

In each of the following tests, as much of a lead acetate solution as corresponded to 0.504 gram lead molybdate, was added to a solution containing also a decigram of a foreign element.

When the solution contained either nickel, zinc, copper, cadmium, magnesium, mercury(ic), arsenic(ous or ic), uranium, or aluminium, no result was obtained, by igniting the precipitate formed as described for pure solutions, which differed in weight from the standard by more than one per cent. Other metals gave the following results:

Cobalt,	-	0.5140.	Strontium,	-	0.5620.
Calcium,	-	0.5600.	Barium,	-	0.6460.

These are elements whose salts form insoluble molybdates. The interference of the cobalt is eliminated by a single re-precipitation; that of the others can be eliminated only by using the 'acid precipitation' and repeating it at least twice.

It has already been remarked (page 85) that in the presence of an excess of lead acetate the most easily filtrable form of lead molybdate is obtained by destroying the free hydrochloric acid, which is keeping it dissolved, by means of ammonium acetate. If a like procedure be followed in the presence of an excess of alkaline molybdate, the lead comes down as a lustrous silky precipitate, somewhat resembling the well-known precipitated manganese-ammonium phosphate. This precipitate can be filtered and washed with the greatest ease.

The colour of the precipitate is yellower than when formed with an

excess of lead acetate, and it invariably contains a little free molybdic acid; less, however, if ammonium molybdate be added gently to the agitated liquid than if added altogether. This error decreases with the excess of molybdate used, so that if the precipitate be re-dissolved in hydrochloric acid, and re-precipitated with ammonium acetate without any further addition of alkaline molybdate, the ideal conditions are almost attained, and the results are very accurate.

Any insoluble lead compound obtained in the course of analysis can be transformed to the molybdate for weighing. The sulphate only is commonly met with, and this after collecting on a small pulp filter and washing with dilute sulphuric acid is treated with an excess of ammonium acetate. Then an excess of ammonium molybdate is added without necessarily straining off the paper, and the precipitated molybdate of lead collected, washed, ignited, and weighed as usual.

#### Direct Estimation of Lead in Alloys.

Decompose the alloy with strong nitric acid mixed with its volume of hot water, evaporate to low bulk (five or six c.c.), but by no means to dryness, dilute with hot water, boil, cool, make up to 250 c.c., and filter off 200 c.c. Measure out a suitable portion of the clear liquid, add ammonium chloride, and enough ammonium acetate to destroy free nitric acid, and precipitate lead as molybdate in the manner already described. As the precipitate often contains a little antimony, or perhaps tin, it is ignited not more strongly than is necessary to burn the paper, and after weighing is dissolved in dilute hydrochloric acid, the solution filtered, and re-precipitated.

Some results obtained as above, and after separating as lead sulphate in the course of a general analysis of alloys containing lead, tin, antimony, and copper, are:

Direct, . . . .	40.00	85.87	51.37 per cent.
Lead Sulphate, . .	40.28	85.88	51.26 „

The procedure just outlined is not suitable for the estimation of small amounts of lead in alloys containing preponderating amounts of tin. A process of quite general applicability is: Proceed as for a complete analysis (page 280) until the sulphides of lead and copper have been digested with nitric acid; then add any lead chloride which may have separated at an earlier stage of the process, and precipitate the lead as molybdate in the presence of ammonium acetate without troubling to separate it, as sulphate, from the copper.



## DIRECT ESTIMATION OF OTHER METALS.

**Copper.**—Several processes for the direct estimation have been investigated, but none have proved quite satisfactory for the small amounts—varying from traces up to three or four per cent.—generally found in white anti-friction alloys.

**Arsenic.**—One or two grams of the alloy are dissolved in hydrochloric acid and potassium chlorate with the application of as little heat as possible. The small excess of chlorine and the arsenious oxide are reduced by a few drops of a strong hydrochloric acid solution of stannous chloride (page 195) and the arsenic precipitated with sulphuretted hydrogen, and estimated as already described. If the alloy is decomposed in the cold, and if neither antimony nor copper are present a dark brown or black insoluble residue indicates arsenic.

**Bismuth.**—This element, which is oftener present as an impurity than as a purposed constituent, is detected by decomposing the alloy with nitric acid, boiling to low bulk, diluting and adding potassium iodide. The characteristic yellow colour not discharged by sulphurous acid indicates bismuth. In the presence of lead a deep red colour appears instead (see page 262).

## GENERAL ANALYSIS OF WHITE-METAL ALLOYS.

That the general analysis of white anti-friction metals of a varied kind according to any method affords ample scope for the operator's initiative is a remark that can be fully appreciated only by those with some experience.

Some writers on this subject attach much importance to a preliminary qualitative analysis and urge that the time thus spent is repaid several times over. We dissent from this. An experienced analyst, working according to the following instructions, will have some notion of the approximate composition of the alloy before the analysis proper is begun; and in unusual cases a second analysis, modified according to the results of the first, enables the work to be satisfactorily done in the least time.

One gram of the finely divided alloy is digested with 20 c.c. concentrated hydrochloric acid below boiling point until action nearly ceases. The residue contains nearly all the antimony, arsenic, bismuth, and copper, if undue contact with air has been avoided. Small crystals of potassium chlorate are now added until the residue is dissolved and the solution has a yellow colour, which is very deep if much copper is present.



Cool the liquid rapidly : if much lead separates as chloride it may be filtered off, washed, and preserved until the portion remaining dissolved has been recovered as lead sulphate. This step is desirable in order to avoid an unwieldy precipitate with sulphuretted hydrogen.

If no lead chloride separates then dilute the solution with two or three times its own volume of water, add tartaric acid up to three or four grams according to the amount of antimony present,<sup>1</sup> neutralize the bulk of free acid with caustic soda, and pour the still clear liquid into fifteen grams of pure caustic soda dissolved in hot water. The mixture is almost perfectly clear, and will be more or less blue according to the amount of copper present.

On looking over the preceding paragraphs it will be seen that the main constituents of most white anti-friction metals have presented themselves in a semi-quantitative form : antimony in the undissolved residue ; lead in the separated chloride ; copper in the blue coloured caustic alkali, and tin by difference.

Pass sulphuretted hydrogen through the warm alkaline solution until by transmitted light it appears clear and the precipitated sulphides are flocculent. A drop of the clear solution should discolour lead paper, thus showing that it contains a small amount of sodium sulphide.

The caustic soda should on no account be saturated with sulphuretted hydrogen, as this would form sulphy-stannates, antimonates, or arsenates, in each of which copper sulphide is soluble. This form of error is widely prevalent in the minds of careful workers, and has given rise to the belief that small amounts of copper, bismuth, etc., cannot be quantitatively separated from alkaline solutions with sulphuretted hydrogen.

The precipitated sulphides of lead, copper, bismuth, iron, etc., are filtered off and washed with a dilute solution of sodium sulphide until the acidified washings show no precipitate of antimony or tin.

Evaporate the filtrate which contains the antimony and tin to about 150 c.c., and add enough hydrochloric acid to precipitate and partly re-dissolve their sulphides. Boil the solution, with the addition of a crystal of potassium chlorate if required, to obtain a clear solution ; then cool and dilute to 200 c.c. A suitable portion of the solution is used for the determination of tin, and the remaining and usually much larger portion used for the determination of antimony by reducing respectively to stannous and antimonious chloride and

<sup>1</sup> If the alloy contains ten per cent. or less of antimony it remains almost entirely dissolved in the caustic soda if no tartaric acid is added. The two or three tenths per cent. precipitated with the lead and copper are recovered during the subsequent operations with the latter metal.

titrating with iodine as on pages 273 and 275. The modifications needed by the presence of arsenic have been already referred to.

The residue is heated, filter and all, with 1.20 nitric acid until the sulphides of lead and copper are decomposed. The paper and sulphur are then filtered off, washed, and ignited: no appreciable residue should be left unless the washing has been imperfectly done. Evaporate the filtrate to low bulk, add sulphuric acid, and continue the evaporation until all nitric acid is driven off, then dilute, allow the solution to cool, filter off lead sulphate, wash with dilute sulphuric acid, transform the precipitate to and weigh as lead molybdate as on page 260.

Neutralize the filtrate with ammonia, add ammonium carbonate, boil and filter. The filtrate contains the copper, which is estimated iodometrically after evaporating to low bulk.

The only element in the residue which needs generally to be estimated is bismuth. Dissolve it in hydrochloric acid, saturate the solution with sulphuretted hydrogen, collect the sulphide of bismuth, dissolve it in nitric acid, evaporate to low bulk, dilute, add potassium iodide, and compare the yellow colour with standards as on page 261.

If small amounts of iron, zinc, etc., which are generally present only as impurities of the main constituents, need to be estimated, then after lead sulphate has been removed the solution is saturated with sulphuretted hydrogen, and the precipitated sulphides of copper and bismuth separated and estimated as before. The filtrate contains any iron, aluminium, nickel, or zinc. When present in very small amounts only, the two former are separated from the latter two with ammonia, and the separate estimation of each element then made in well-known ways. It must not be forgotten that the caustic soda used frequently contains more iron and aluminium than exists in the alloy.

TYPICAL ANALYSES.

	Thurston's White Metal.	Babbitt's Metal.	Tandem Metal.	Magnolia Metal.	Commercial Tin.	Type Metal.	Antimonial Leads.	
Tin, -	71.0	46.03	4.16	5.00	98.67	27.55	0.56	2.50
Antimony, -	24.0	9.16	11.12	14.82	0.60	28.41	11.72	34.00
Lead, -	—	40.24	84.21	80.04	0.44	40.59	85.91	61.40
Copper, -	5.0	4.27	—	0.10	0.15	2.90	0.41	0.84
Bismuth, -	—	—	trace	0.19	0.06	0.10	—	—
Arsenic, -	—	0.17	—	—	0.08	0.40	0.85	0.66
	100.00	99.87	99.49	100.15	100.00	99.95	99.45	99.40

## PART XI. THE MICROGRAPHIC ANALYSIS OF STEEL.

SORBY was the first to recognize the value of the microscope as a means of determining the structure of steel, and his invaluable work, which dates back nearly to 1860, inaugurated a branch of metallurgical research which, although it lay dormant for many years, has recently attained to great importance.

It is exceedingly difficult to evolve order out of the confusing and conflicting array of observations that have been made of late years, and it is beyond the scope of this work to attempt the task ; enthusiasts in this subject are referred to the pages of the *Iron and Steel Institute's Journal*, the *Metallographist*, and to the bibliography which accompanies this section. The authors propose rather to give instructions for the preparation of samples for microscopic examination, and to describe briefly a few typical structures without appealing to any theory respecting the 'nature' of steel.

It is now recognized that a steel may actually break down in use, even although its chemical analysis and mechanical tests are perfectly satisfactory, so that in such cases the microscopic method of examination becomes a most invaluable accessory. At the same time it is perhaps advisable to point out that the indications of microscopy should not be accepted as final ; complete knowledge of chemical constitution, mechanical tests and heat treatment, must be correlated with that of the ultimate structure as revealed microscopically.

All metals have a structure comparable with that of an igneous rock, and the terminology of petrography has happily been applied to the constituents of steel. Before these constituents can be viewed and recognized through a microscope, however, the specimen must undergo a special preparation. As a general rule, this consists in the production of a plane polished surface, which is then subjected to some etching process so as to develop the structure. No two metallographists use

exactly the same means of preparation, and the appended description of these operations is substantially that of the methods in use in the metallographic laboratory of the Sheffield University College. These methods are based on those pursued by Sorby, whose preparations, made nearly 40 years ago, and to which the authors have been privileged to gain abundant access, have not since been equalled.

### PRELIMINARY PREPARATION.

It is evident that one plane surface only is required for examination, but if time permit, and whenever possible, a specimen should have two parallel plane faces. A convenient form is that of a circular disc about half an inch in diameter and from one-tenth to one-eighth of an inch in thickness. When some other shape is submitted for examination, it is advisable to remove, if there are any, all sharp corners from the sample in order to eliminate the liability to damage of the polishing blocks. After cutting the specimen with a hack saw or in the lathe, the machined piece should be rubbed on the face to be prepared along the surface of a dead-smooth file.

Very hard material such as white iron cannot be handled in this manner very easily, and a broken fragment of the sample is therefore selected and a plane face secured by grinding on an emery wheel. Wires and thin plates should be suitably supported.

It is worthy of note that accurate knowledge of some structures is only obtainable by making, from the same piece, three sections in three planes mutually at right angles.

#### Methods of Polishing.

Two pieces of hard wood, about 8" × 6" × 1", are carefully planed, and upon one face of them are glued two strips of English emery cloth marked *O* and *OO* respectively, adhesion being secured by pressure applied for several hours. Before use, it is advisable to scour off as much as possible of the loose emery. After leaving the dead-smooth file, the specimen is rubbed backwards and forwards along the surface of the *O* block until all the file marks and any other irregularities are obliterated. It is then transferred to the *OO* block and, by a similar movement, the scratches left by the first rubbing are eliminated by substituting the finer ones induced by the second block. It is evident that the complete removal of the 'heavier' scratches can be best seen by making the lighter ones at right angles to them. The subsequent treatment consists in a complete

removal of scratches by means of a rapidly revolving block or disc, the surface of which is dressed with various materials. There are several different machines on the market for effecting this circular polishing, the simplest of which require little power. Fig. 20 shows the type of block used by the authors; a battery of six of these is driven at varying speeds by means of a small motor. It will be seen that each one consists essentially of the tapering block *A* made of brass, over the surface of which the polishing medium is tightly stretched by means

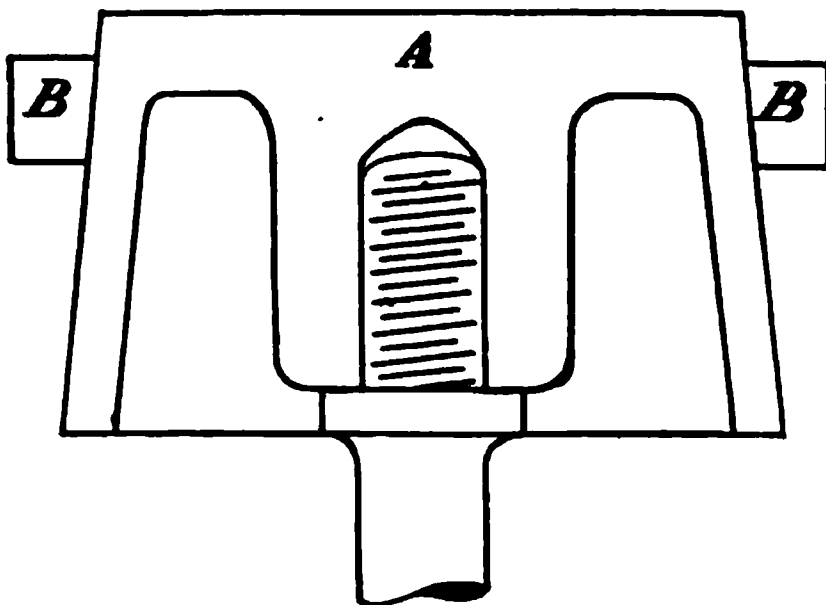


FIG. 20.

of the brass annulus *BB*. French emery papers, *000* and *0000*, very quickly pave the way to the final polishing. This is done first on diamantine powder, well rubbed into the stretched membrane of parchment or chamois leather, and lastly on jeweller's rouge rubbed into the surface of a stretched piece of untanned kid skin. Both powders can be purchased, but may be prepared by the ignition of ammonium alum and ferrous oxalate respectively.

The time occupied in polishing a specimen depends chiefly on its hardness. Hard steels may be prepared in 10 to 15 minutes, but soft materials occupy more time. During the circular polishing of such soft materials, it is better to apply gentle rather than vigorous pressure. The specimens may be held stationary on the revolving block by the fingers; two or three at a time may be manipulated by attaching a finger to each with a tiny drop of Canada balsam, and the polishing process may be hastened by a circular movement of the hand, accompanied by pressure, in the opposite direction to the motion of the block.

Osmond has described a method of polishing and etching combined. This 'polish attack' is accomplished by means of precipitated calcium sulphate and aqueous extract of liquorice root applied to the surface of parchment. The same results are yielded by a two per cent solution of ammonium nitrate crystals.

#### Etching the Specimens.

As seen under a magnification of about 300 diameters, the polished specimen, finished on rouge as described above, presents in many

instances a striking appearance. The ferrite areas of a mild steel, for example, are usually blue in colour and the pearlite areas brown, whilst here and there a particle of dove-grey sulphide of manganese can be distinguished. From these latter as centres, the polishing has created straight radiating white tracks, as if minute particles of the sulphide had been detached and had scored the surface of the metal. The boundaries of the constituents are not, however, sufficiently well marked, and it is necessary, for most steels, to etch the polished specimen.

In addition to ammonium nitrate and aqueous infusion of liquorice, commercial tincture of iodine diluted with four times its volume of alcohol is frequently used. This solution is rubbed gently over the polished surface with the tip of the finger, and the operation repeated as often as examination under the microscope shows it to be necessary. In spite, however, of the expressed opinions of many metallographists to the contrary, the authors believe that the best etching liquid for steels is dilute nitric acid; 20 to 30 c.c. of nitric acid (1·20) diluted with water to 1000 c.c. will be found to yield admirable results.<sup>1</sup>

Before etching, it is advisable to see that the polished surface of the section is clean; absolute freedom from grease or finger marks is imperative. The specimen is put in a small rectangular glass trough and rapidly covered with the acid, the progress of the etching being observed through a small pocket lens. Exact rules cannot be formulated for the length of time required; it is easy enough at any moment to stop the etching, and after washing and drying to examine the piece under the microscope. A few experiments of this kind with steels of known carbon contents soon enable an observer to determine the end of the operation without resorting to these periodical stoppages. Two or three minutes' contact with the acid develops the structure of pearlite, but a longer time or stronger acid are required to determine the shape and size of iron crystals. After thoroughly washing away the acid from the etched specimen in a stream of water, a bath of absolute alcohol and rapid drying complete the preparation.

The clearness of the structure is in many cases much improved by very gentle rubbing with a small piece of soft clean kid skin. The etching of a hardened steel with dilute nitric acid, which should be considerably stronger for such steels, results in the deposition of a fine black carbonaceous film on the surface. This should be removed by rubbing with the tip of the finger whilst the washing is in progress.

<sup>1</sup> A saturated solution of ferric chloride containing ten per cent. of hydrochloric acid is a very good etching medium for steels.

### Heat-Tinting.

It is desirable in certain cases to substitute a 'heat-tinting' process for the etching. This is done by rubbing the polished specimen vigorously with a clean leather and, whilst warm, placing it on an iron plate underneath which a small bunsen flame is burning. The oxidation colour tints develop at different rates on the different constituents, so that these can be readily identified under the microscope. The heat-tinting is stopped at any desired stage by quenching the specimen in mercury. Exact instructions for this most interesting process are given by Stead in the *Iron and Steel Institute's Journal* for 1900, Part II., page 137. In this connection, it may be pointed out that the method constitutes the only reliable means for the microscopic identification in steels of the element phosphorus. The amount of phosphorus in steels is considerably below that at which it forms a definite micro-constituent, for although a portion of the iron phosphide may be thrown out of solution by the carbon of hard steels, most of it remains in solid solution. Pearlite areas containing phosphorus take the tints more rapidly, however, than ordinary pearlite.

### Rapid Method of Preparation.

The time occupied in the polishing and etching of a section constitutes a serious drawback to the employment of the microscopic method of research in a busy steel-works, particularly when the elaborate system of polishing recommended by some metallographists is practised. It is with pleasure therefore that the authors direct attention to a rapid method of preparation described by Arnold in *Nature*, lxiii. p. 613, by the use of which a steel is ready for examination within five minutes of its being machined from the piece.

The section is rubbed, as described previously, first on *O* and then *OO* emery cloth, and is then etched at once. This is done by covering the sample with nitric acid, s.g. 1.20 for about a minute; more strictly speaking, until bubbles of gas make their appearance just after the surface has blackened over. The contact with the acid is long enough to bring about an almost complete removal of the scratches, and the structure is sharply defined.

For ordinary purposes the method is suitable for nearly all commercial steels. The laminated pearlite which is so typical a constituent of well-annealed steels containing very little manganese, appears to be broken up by this rather severe treatment, so that for such steels the method is not so suitable.



### Mounting, etc.

When the specimen has parallel plane faces, it may easily be attached to the ordinary glass slide by means of Canada balsam or 'plasticene.' It should then be thoroughly examined and, if required, a permanent record of the structure obtained, by drawing or photography, before the etched surface begins to rust. The surface may then be protected by a coating of paraffin wax dissolved in benzole; this can easily be removed subsequently by an application of the solvent. A solution of gun-cotton in amylacetate, which is sold under the names of 'zapon,' 'silver varnish,' etc., also constitutes a serviceable protective covering.

The authors have practised very largely both of the following methods of mounting and preserving the etched specimens:

1. The section is attached to the glass slide by means of Canada

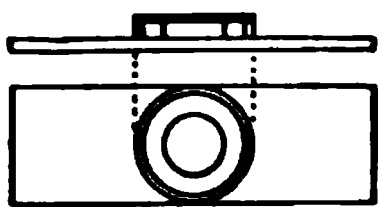


FIG. 21.

balsam (or a solution of it in benzene), and a brass ring of exactly the same thickness as the specimen is similarly fastened. The rim of the brass ring is then smeared lightly with the balsam and a cover slip put on. Fig. 21 shows the arrangement.

2. After attaching the specimen to the slide, the etched surface is smeared over with Canada balsam which has been thinned slightly with benzene. The cover slip is then put on and the mounted specimen set aside to dry. There is no serious inconvenience occasioned by the thin layer of balsam, although it is advisable, when either of these methods is used, to photograph the specimen before putting on the cover.

In mounting irregularly-shaped samples neither of the foregoing methods, for obvious reasons, can be used. In such cases the following procedure, described by Stead, will be found eminently satisfactory, and it may evidently be used for flat sections. "The polished face of the section is placed on a piece of plate glass, and over it a short brass cylinder, accurately turned, of such depth that the back of the specimen does not stand above the cylinder. A piece of plastic wax (plasticene) is stuck upon the centre of a glass microscopic slide, and this is then pressed upon the section until the glass slide comes in contact with the brass ring. The specimen adheres to the wax, and the mounting is complete."

### Microscopic Accessories: Photography.

A magnification of about 300 diameters is sufficient for nearly all purposes, and this is easily secured by a one-sixth of an inch objective. Occasionally a more powerful objective is useful, but for works' purposes



may be considered unnecessary. In addition to the 'sixth,' however, the microscope should be equipped with a one-inch objective so as to give a magnification with the eyepiece, of from 40 to 60 diameters.

The examination of opaque objects necessitates their illumination from above when the tube of the microscope is vertical, and a brief description of the method of illumination may be found useful.

The distance of the low-power objective from the focussed object is great enough to admit a reflecting arrangement between it and the object. A Nachet prism or a parabolic mirror (Fig. 22) may be used; the latter is attached by simply slipping it over the tube. The parabolic mirror carries also a small plane mirror set at an angle of  $45^\circ$ , which can be swung in and out of position as shown by the dotted lines. Using the parabolic mirror only, much of the light striking the specimen will be reflected from its surface without actually entering the microscope; the plane mirror converts this oblique into a direct illumination. The two kinds of illumination are very useful in the identification of hard constituents, such as cementite.

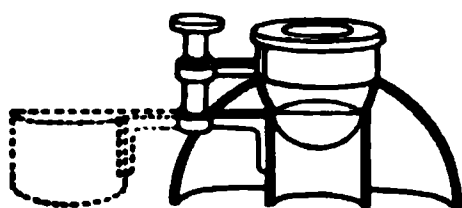


FIG. 22.

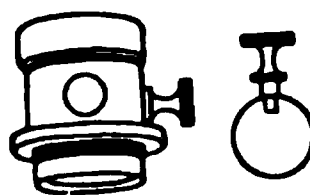


FIG. 23.

With the high-power objective, a direct illumination is obtained by means of a thin glass reflector—an ordinary cover slip serves admirably. This is attached (Fig. 23) to a small screw, which fits loosely into a hole either in that part of the tube carrying the objective or in an auxiliary piece into which the objective can be screwed.

The ordinary incandescent gas will be found very suitable as a source of light, with or without the intervention of a condenser. If an image of the incandescent mantle is seen to obscure the field, the light should be made to pass through a screen of ground glass before entering the microscope.

In photographing a section the lens of the ordinary camera is screwed off and the camera then put over the eye-piece of the microscope. The latter may be placed horizontally or vertically; if the vertical position is used it is not difficult to arrange the camera so as to permit of swinging it into position after having selected a suitable field for re-production. The focussing is best done by removing the ordinary ground glass screen of the camera and substituting a piece of ordinary plate glass; an extra eye-piece is then held on the plain glass screen, and the image viewed

by its means. Details concerning time of exposure, etc., are matters for individual experiment.

### THE MICRO-STRUCTURE OF STEEL.

The micro-structure of steels and irons is determined not only by the amounts of the constituents other than iron, but also by the thermal and mechanical treatment to which they have been subjected.

Our present knowledge of steel micrography has necessarily been obtained synthetically, and a study of the effect of the combination with

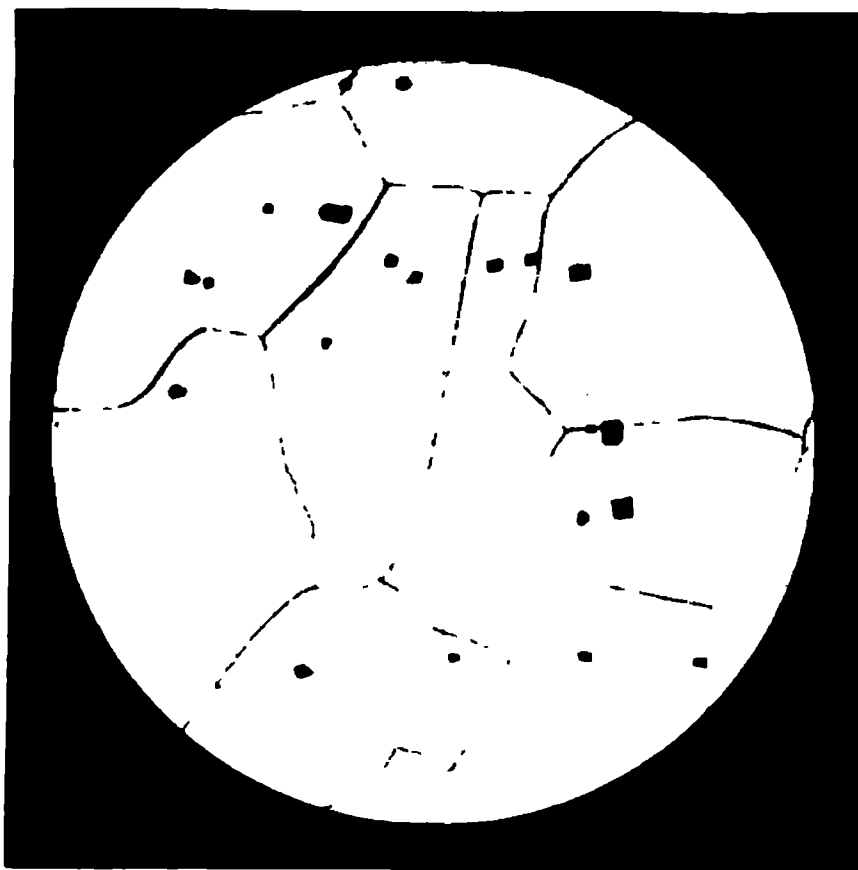


FIG. 24.—Swedish Bar Iron. (Transverse section,  $\frac{1}{4}$  in. objective.)

iron of gradually increasing amounts of carbon, whilst the other elements are kept as small in amount as possible, constitutes the best method of dealing with the subject. The authors are of opinion that Arnold's paper on "The Influence of Carbon on Iron." (*Proc. Inst. Civil Eng.* cxxiii. p. 127, 1895) is one of the most valuable contributions to this branch of metallurgical research, and the reader may recognize its imprint in the following pages.

Figs. 24 and 25 exhibit the micro-structure of the purest Swedish bar iron; the former is a transverse, and the latter a longitudinal section of the same bar. Both sections exhibit roughly polygonal crystals of practically pure iron, micrographically termed *ferrite*, whilst the transverse section shows rounded dots and the longitudinal section drawn-out threads of slag. Fig. 26 shows the structure of a specimen of the best English wrought iron; the amount of slag is much greater than in the pure Swedish material. All three sections were etched

sufficiently long with dilute nitric acid to develop the junctions of the ferrite crystals.

Parenthetically it may be observed that the presence of slag,<sup>1</sup> which generally shows in unmistakable masses, constitutes a means of



FIG. 25.—Swedish Bar Iron. (Longitudinal section.  $\frac{1}{2}$  in. objective.)

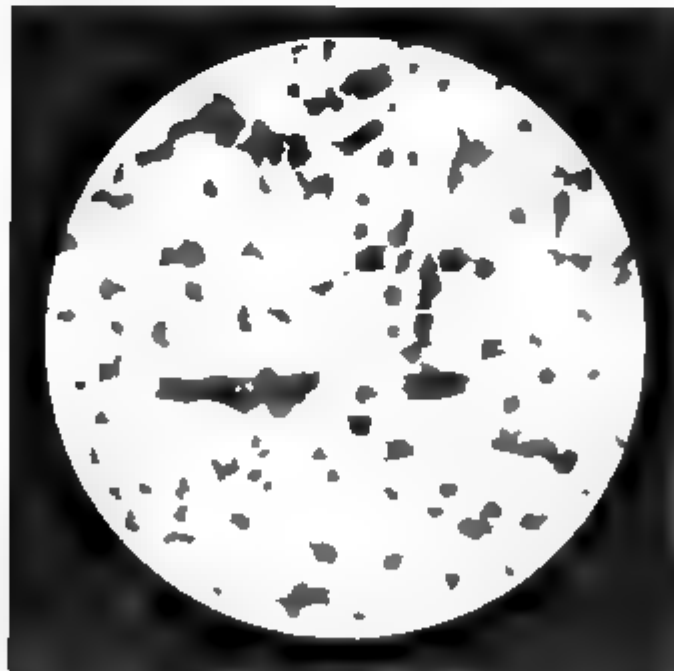


FIG. 26.—English Puddled Iron. ( $\frac{1}{2}$  in. objective.)

<sup>1</sup> Slag and sulphide of manganese of iron may be distinguished from each other by the application of a dilute acid solution of cadmium sulphate (Report of the Committee—appointed by the Board of Trade—on "The Loss of Strength in Steel Rails through use on Railways," 1900).

distinguishing wrought iron from steel. Wrought iron often contains as much carbon as very mild steel, but the latter very rarely contains slag in appreciable amounts.

### I. Pure Iron-Carbon Steels.

(a) **Normalized.**—Fig. 27 shows the structure of a steel containing nearly 0.5 per cent. of carbon. The section was cut from a round bar which had been forged from an ingot of crucible steel of the highest degree of purity, and the structure is typical of all mild steels, which

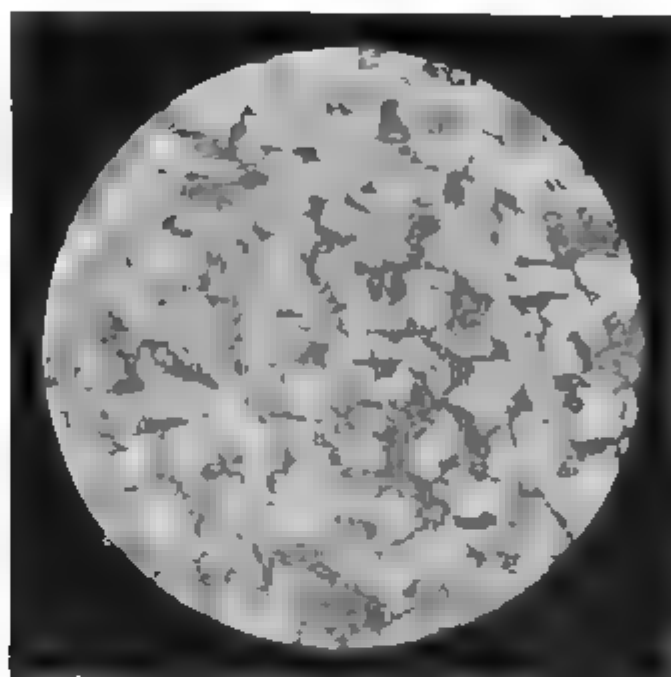


FIG. 27. ~0.5 per cent. Carbon. ( $\frac{1}{8}$  in. objective.)

after being heated to full redness are allowed to cool in air. Such steels may be conveniently termed "normalized." In addition to ferrite, which etches nearly white, there is a dark-etching constituent, micrographically termed *pearlite*. This consists, in steels containing negligible amounts of foreign elements, of carbide of iron ( $\text{Fe}_3\text{C}$ ) in intimate association with iron itself, and contains practically 0.9 per cent. of carbon. This corresponds to 13 per cent. of the carbide and 87 per cent. of iron. In normalized steels pearlite has, when viewed by direct illumination, the granular appearance depicted in the figure.

It follows that 0.9 per cent. of carbon combined with iron yields a steel which consists practically of pearlite only. Such a steel is shown in Fig. 28. When the amount of carbon exceeds 0.9 per cent. the excess makes its appearance as a new constituent micrographically termed *cementite*. This is the definite chemical compound  $\text{Fe}_3\text{C}$ ; it is very hard, and appears under the microscope as a very bright con-

stituent. Fig. 29 shows such a steel containing about 1·4 per cent. of carbon. The cementite may, in certain cases of well-forged steels,

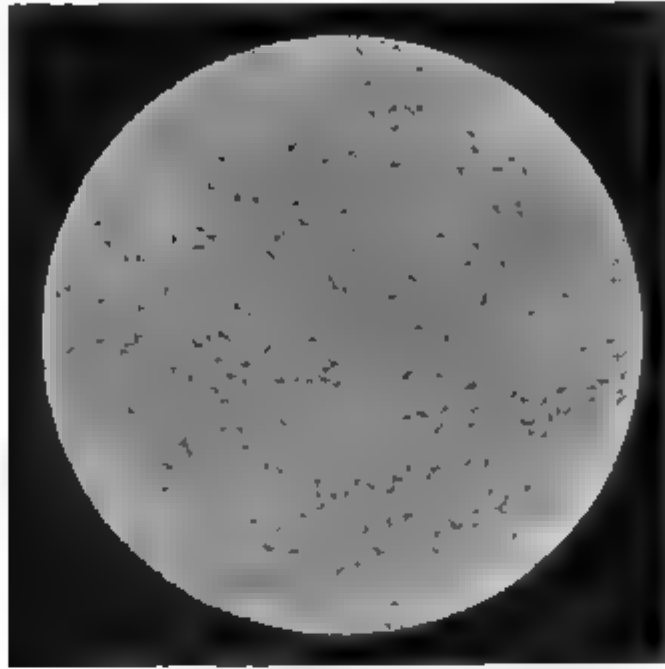


FIG. 28. 0·0 per cent. Carbon. ( $\frac{1}{4}$  in. objective.)

segregate into rounded masses or dots, giving the micro-section an appearance very much resembling that of a mild steel containing free ferrite.

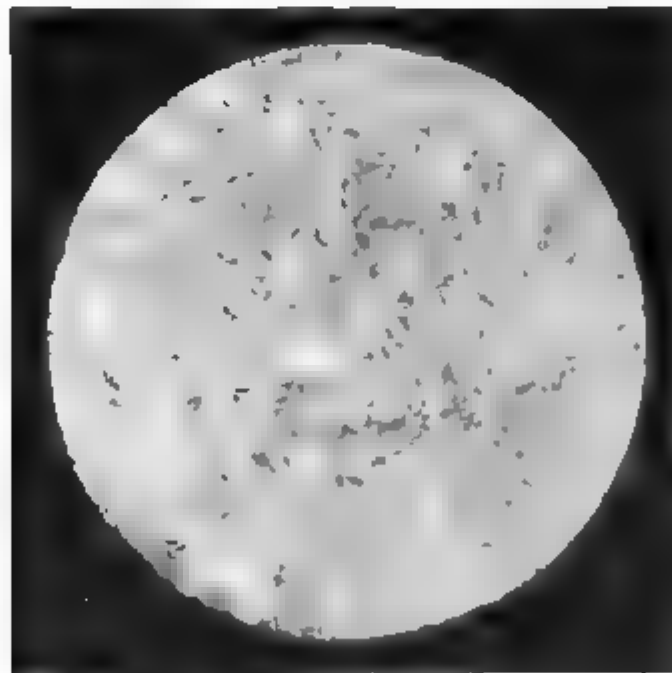


FIG. 29.—1·4 per cent. Carbon. ( $\frac{1}{4}$  in. objective.)

We thus arrive at the generalization that the micro-structure of steel containing less than 0·9 per cent. of carbon consists of ferrite and

pearlite, whilst steels containing more than 0·9 per cent. of carbon consist of pearlite and cementite, and steels containing 0·9 per cent. of carbon exhibit pearlite only. The last of these are sometimes termed 'saturated' steels.

(b) **Annealed.**—A steel is annealed by slowly heating up to full redness and, after maintaining this temperature for some time, slowly cooling again; the steel throughout the operation being shut off practically from the air. The time occupied in actual practice by the annealing process is variable, and whilst there can be no doubt that excessive annealing does no good and may do harm, a good proportion of the unsatisfactory steel castings is accounted for by erring on the other side.

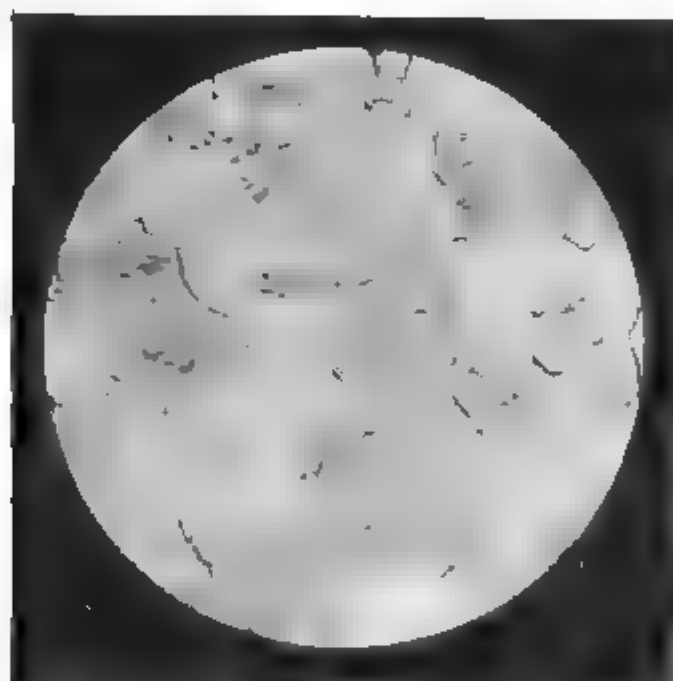


FIG. 30. 0·5 per cent Carbon. ( $\frac{1}{4}$  in objective.)

The most striking change induced in such steels as the three already described, by annealing them, is exhibited by the pearlite. The components of this constituent are separated and re-arranged in more or less parallel plates constituting the true "pearly constituent" first described by Sorby. This banded structure is highly characteristic of slowly cooled steels; very light etching with the weakest nitric acid develops interference colours on such steels, due to the presence of the laminated pearlite. Figs. 30, 31, and 32 show the micro-structures of annealed iron-carbon steels containing 0·5, 0·9, and 1·3 per cent. of carbon respectively. The etching of the mildest of these was stopped before the junctions of the ferrite crystals developed.

The section of the 'saturated' steel will be seen to consist almost entirely of 'true' pearlite. It may happen in some cases, however,

that the segregation of the constituents of pearlite during the annealing process passes beyond the phase of lamination, resulting in the pro-

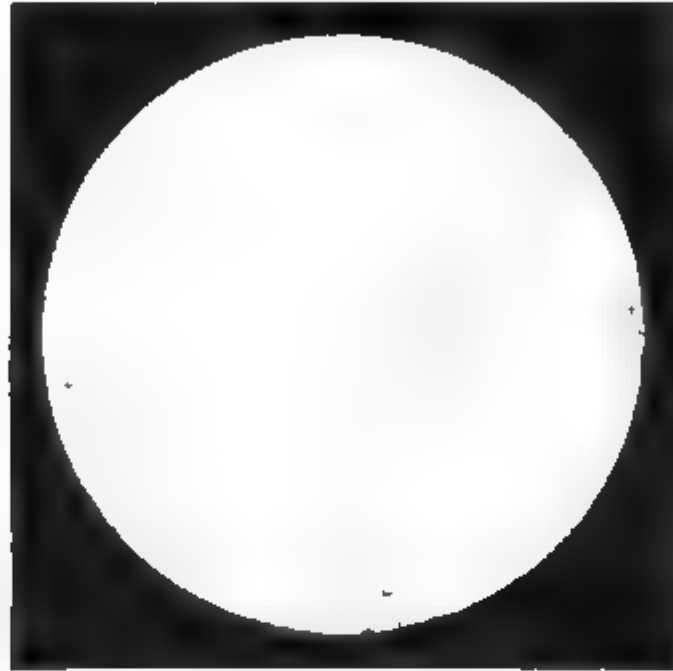


FIG. 31. 0.9 per cent. Carbon. ( $\frac{1}{8}$  in. objective.)

duction of isolated patches of cementite. This is shown to some extent in Fig. 30, and it is very often noticeable in cemented bar steels. The precise conditions under which well-laminated pearlite is formed

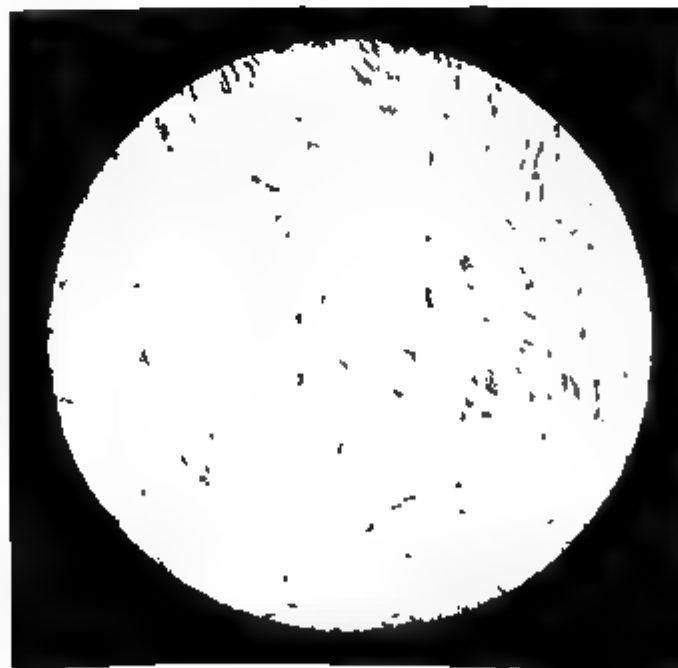


FIG. 32.—1.3 per cent. Carbon. ( $\frac{1}{8}$  in. objective.)

have not yet been satisfactorily determined, nor have those under which the phenomenon mentioned in the following paragraph takes place.

With 'super-saturated' steels in particular, it may happen that free carbon actually separates during the annealing process, and we then encounter a new micro-constituent in the form of *graphite*.<sup>1</sup> This is

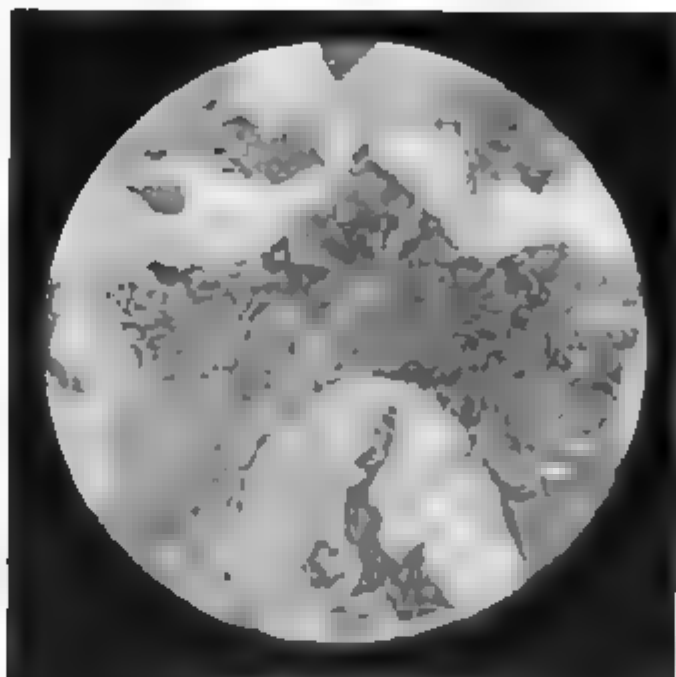


FIG. 33.—1.8 per cent. Carbon. ( $\frac{1}{4}$  in. objective.)

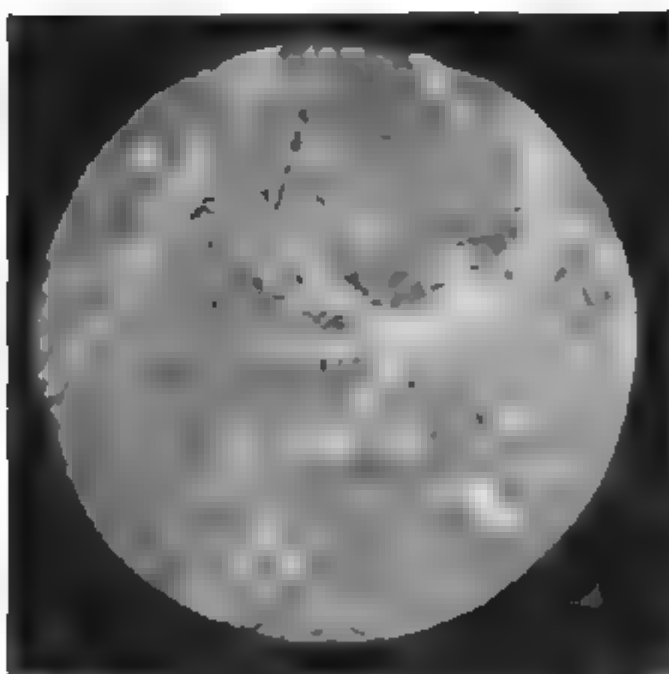


FIG. 34.—1.8 per cent. Carbon. ( $\frac{1}{4}$  in. objective.)

illustrated in Fig. 33 which represents the structure of an annealed steel containing 1.80 per cent. of carbon. Figs. 34 and 35 are respectively high and low power micrographs of the same steel as cast.

<sup>1</sup>Also called *annealing carbon*. It is the 'temper-carbon' of Ledebur—see page 21.



It will be noticed that nearly all the graphite is located in the ferrite areas.

The separation of graphite from hard steels during rolling is a not uncommon occurrence, and is often the result of rolling at too low a temperature.

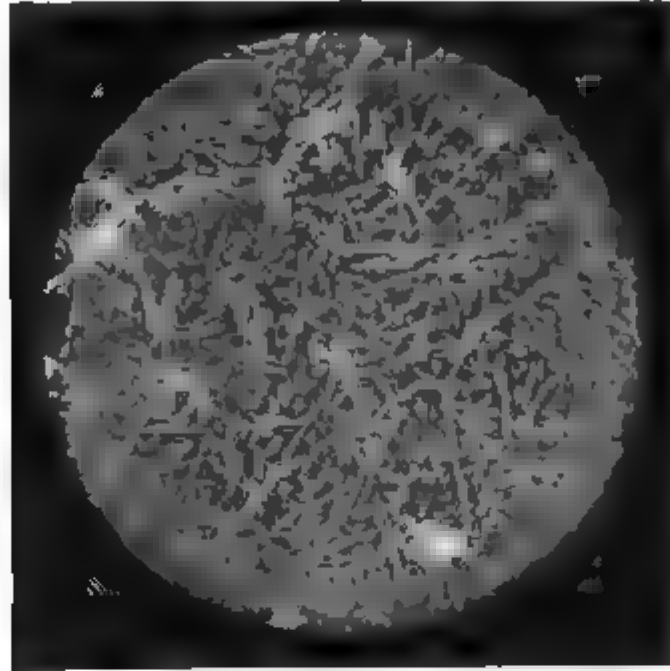


FIG. 25.—1.8 per cent. Carbon. (1 in. objective.)

(c) **Hardened.**—The authors confess to a feeling of diffidence in handling this part of the subject. At the time of writing (March, 1902) the metallographic nomenclature of hardened steels and their actual micro-structure are matters of controversy. The brief account which follows embodies the results of the authors' personal observations, and the opinions expressed have been formed from them; these opinions will be recognized as being at variance with those of many eminent metallographers.

Pure iron-carbon steels, quenched at the lowest temperature that will confer flint hardness on the 'saturated' and 'super-saturated' members of the series, that is, quenched at the temperature employed by the best skilled hardeners of tool steel, contain a new micro-constituent which has been conveniently termed *hardenite*. In addition, the mild steels contain structurally-free ferrite, and the super-saturated steels cementite. It is evident therefore that hardenite may be considered as pearlite that has been heated and afterwards quenched so as to give its maximum degree of hardness. As previously stated, the etching of a hardened steel with nitric acid develops a fine carbonaceous deposit on the face of the section. On gently rubbing this away, examination under the microscope reveals the hardenite as a dark, homogeneous, and

apparently structureless body. It is intensely hard and very unstable. It is the sub-carbide of Arnold. The accompanying figures 36, 37, 38, and 39 represent the micro-structure of specimens of properly hardened steel.

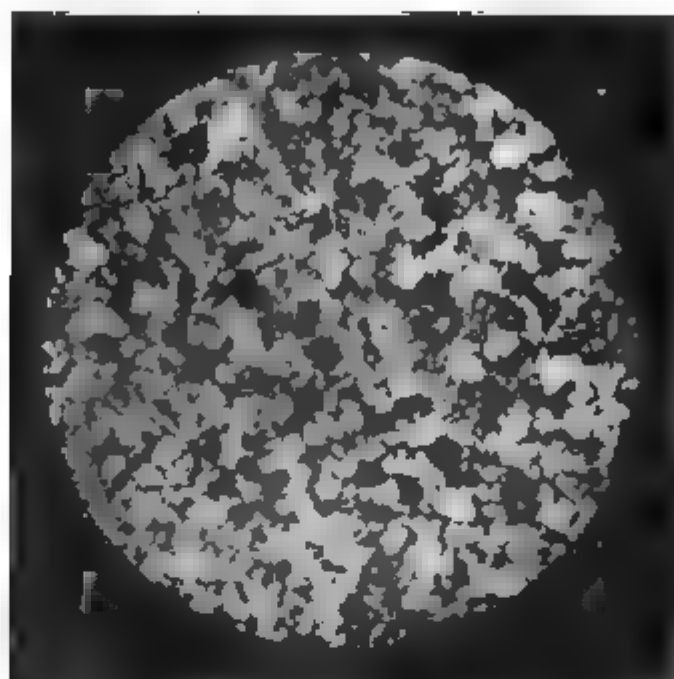


FIG. 36. 0.3 per cent. Carbon. ( $\frac{1}{4}$  in. objective.)

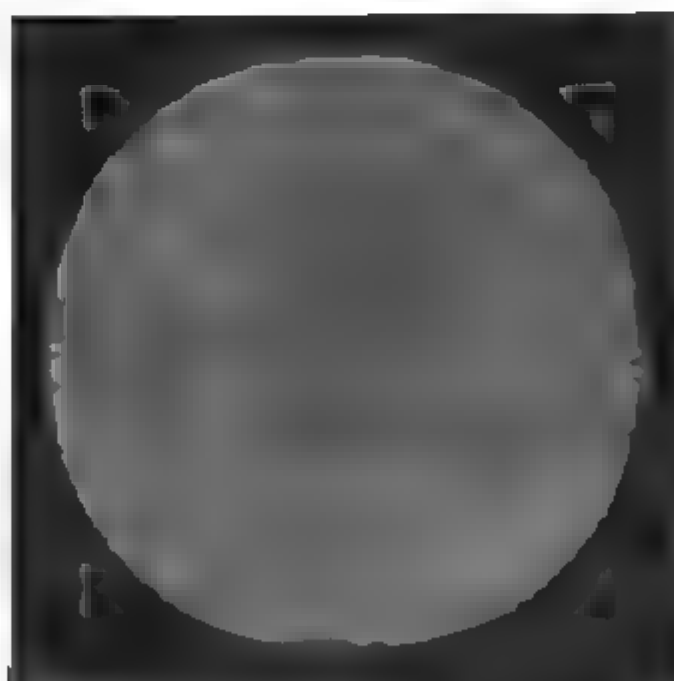


FIG. 37. 0.9 per cent Carbon. ( $\frac{1}{4}$  in. objective.)

Small specimens of steel that are very suddenly quenched from temperatures exceeding  $1000^{\circ}\text{C}$ . yield a structure called *martensite*. This consists of a system of interlacing needles, but martensite can scarcely be called a definite micro-constituent, as its composition varies

in carbon content from 0.1 per cent. to nearly 2 per cent., according to some authorities; its hardness varies too from about 5 to more than 7. The needles may be conveniently termed *martensite structure*.

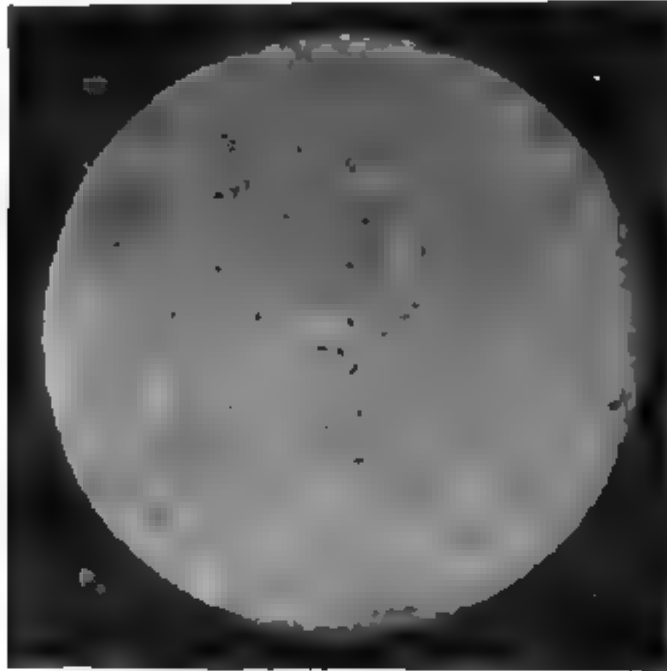


FIG. 38.—1.5 per cent. Carbon. ( $\frac{1}{4}$  in. objective.)

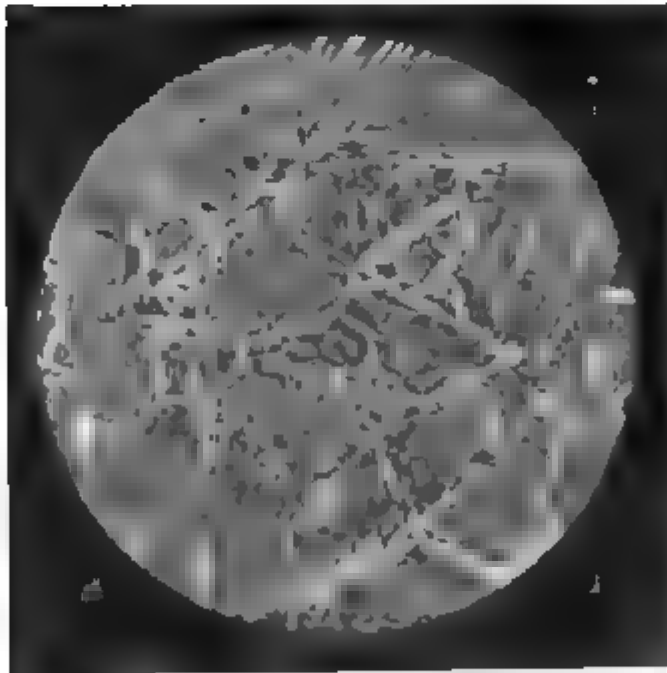


FIG. 39. 1.7 per cent. Carbon. ( $\frac{1}{4}$  in. objective.)

In connection with this part of our subject a brief reference to two other constituents, which Osmond has called *sorbite* and *troostite*, becomes necessary. These are supposed to be recognized by certain etching peculiarities, and the former is described as representing a zone of

transition<sup>1</sup> between ferrite and cementite in unhardened steel and between cementite and martensite in quenched steel, whilst the latter is described as existing in steel quenched during the critical points and is also a transition form between martensite and ferrite.

Lastly, a brief reference to another micro-constituent of quenched steel must be made; it is termed *austenite*. If certain special material formed by subjecting small bars of ordinary commercial dead-mild steels to cementation, until they hold about 1·7 per cent. of carbon, be rapidly quenched from a temperature exceeding 1000° C., a broken sample after grinding on an emery wheel, polishing and etching, sometimes exhibits under the microscope a white angular structure (austenite) on a dark ground of martensite structure. Austenite is stated to be softer and less magnetic than martensite or hardenite, the hardnesses having been compared by drawing the point of a needle across the etched face of the section.

The loss of magnetic properties may not be unconnected with the cracking generally exhibited by such material after this severe treatment. Moreover, the needle test for discriminating between the hardness of martensite and austenite is by no means an ideal one. The hardnesses of two needles from the same packet are not necessarily identical; one may be as low as 6 and the other more than 7. And, further, it is by no means easy to compare the scratches on martensite and austenite, as the former etches nearly black and the latter white. When it is remembered that an ordinarily hardened steel, ten per cent. below saturation, will not retain a good cutting edge, the fact that a sample prepared (for exhibiting austenite) according to the specified instructions, and containing 50 per cent. of that constituent, would scratch quartz at any and every part of the section, is not easily reconciled with the properties supposed to be associated with this constituent.

The opinions expressed above may not, as already indicated, meet with very much favour. The authors' aim throughout, however, has been to make this section useful to practical workers, and so far as they know, the conditions under which martensite and austenite are formed do not obtain in practice, whilst sorbite and troostite are too much of the nature of *rarae aves* to merit much consideration here. Diagrams, illustrating austenite and martensite structures will nevertheless be found at the end of this section.

<sup>1</sup> *Metallographist*, vol. i. p. 37

## II. Manganiferous Steels.

The main facts stated above are applicable, with slight modifications, to the ordinary manganiferous steels of commerce. The amount of manganese in good crucible steel is rarely more than 0·35 per cent.,

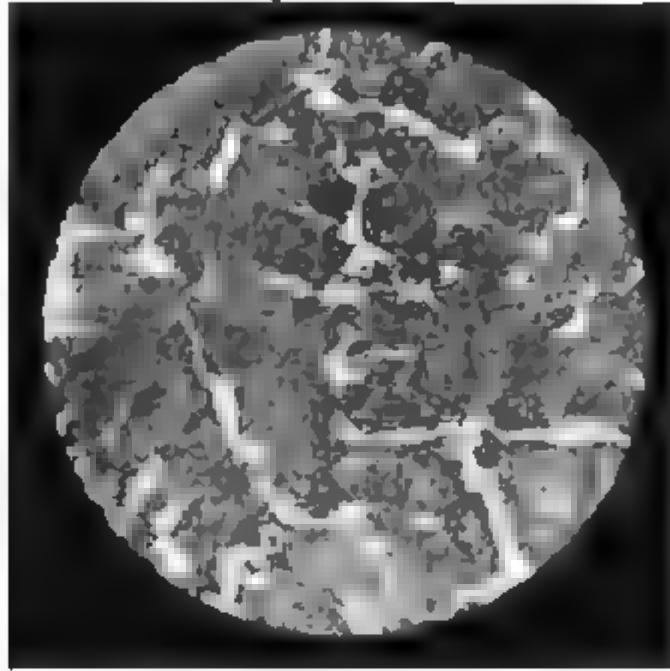


FIG. 40.—Steel Rail. Carbon, 0·37; Manganese, 1·00. ( $\frac{1}{8}$  in. objective.)

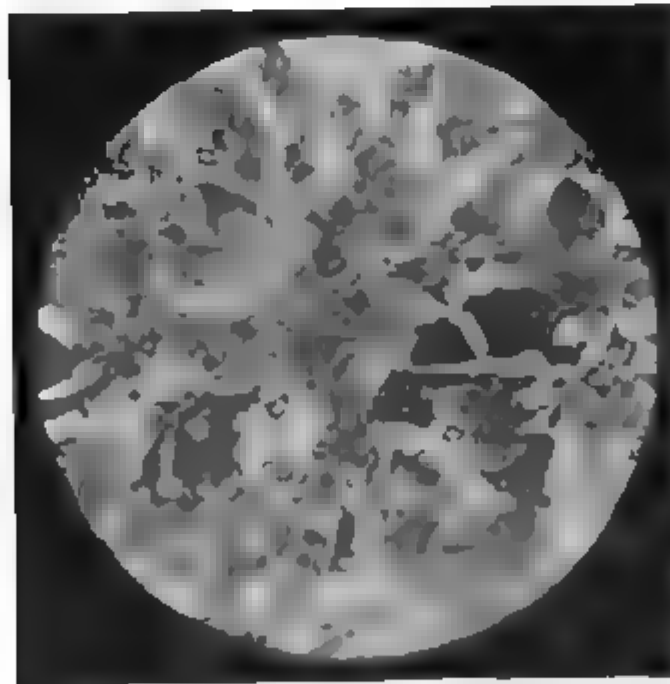


FIG. 41.—St. Neot's Rail. Carbon, 0·50; Manganese, 0·51. ( $\frac{1}{8}$  in. objective.)

in acid open hearth steel about 0·5, and in Bessemer steel about 1·0 per cent. The tendency of this element seems to be, micrographically, a lowering of what has been termed above the saturation point. The

pearlite areas of an etched micro-section of a manganiferous steel therefore are greater than in a pure iron-carbon steel of the same carbon contents. This is shown by the accompanying figures 40 and 41.

The whole question of the constitution and properties of the double carbides of iron with the metals used in steel-making requires thorough investigation: from a metallographic point of view, in particular, present-day ignorance may be safely termed colossal.

Manganiferous pearlite, in a steel etched with dilute nitric acid, is distinctly darker in colour than pure pearlite. There seems further to be a decided tendency during annealing to the suppression of the formation of true or laminated pearlite in manganiferous steels. It is, as a matter of fact, much more common to see no lamination in the pearlite areas of a highly-manganiferous annealed steel than to find it.

The sulphur of an ordinary steel is generally in chemical union with the manganese and not with the iron. Manganese sulphide, for which no micrographic term has yet been adopted, is recognized readily by its occurrence in rounded spots of a dove-grey or lavender colour. (The section of the St. Neot's rail shows these sulphide particles.) This is noticeable before as well as after etching; the spots in an etched specimen are frequently surrounded by a coloured halo. In steel rolled from a high temperature the manganese sulphide is found in elongated threads when a vertical longitudinal section is examined.

### III. Steel Castings.

The micro-structure of steel as cast differs from that of forged and annealed steels in the arrangement of the ferrite and pearlite. This difference is particularly noticeable in mild castings, as a glance at the accompanying figures (42 and 43) will show. The pearlite and ferrite are seen to be arranged in lattice form. Fig. 43 also shows a streak of a brown body generally found in the ferrite areas. There can be no doubt that this body contains sulphur, and from the fact that in highly siliceous castings the number of these thread-like bodies is very considerable, it is probable that the substance is a sulpho-silicide of iron. Fig. 44 shows an example of a highly siliceous steel casting, and furnishes a case in point.

The flame annealing to which steel castings are subjected effects not only a re-arrangement of the 'pattern' of the micro-structure, but probably also decomposes the sulpho-silicide with absorption of the silicon into solid solution with the iron. The structure of a well-annealed steel casting is well shown in Fig. 45, from which it will be seen that the pearlite and ferrite areas become rounded and the sulpho-

silicide streaks disappear, being replaced by small globules, which probably contain all the sulphur and none of the silicon of the original substance.

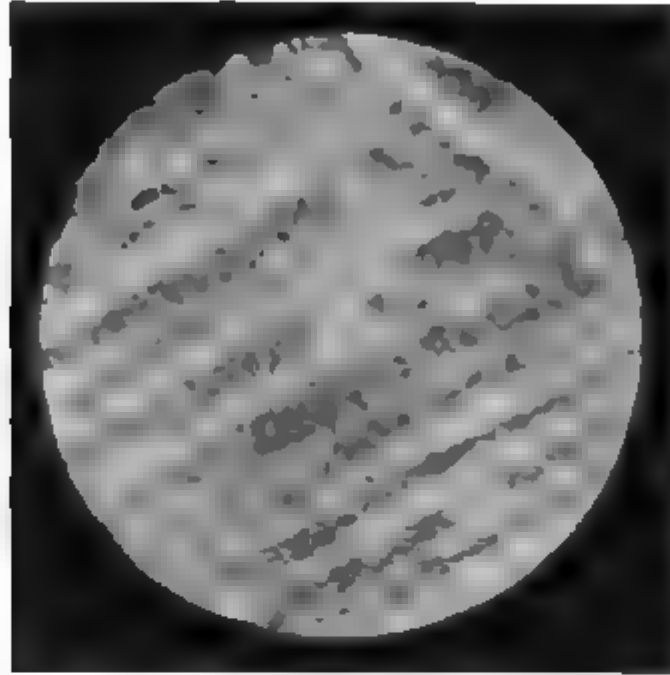


FIG. 42.—0.4 per cent. Carbon. ( $\frac{1}{4}$  in. objective.)

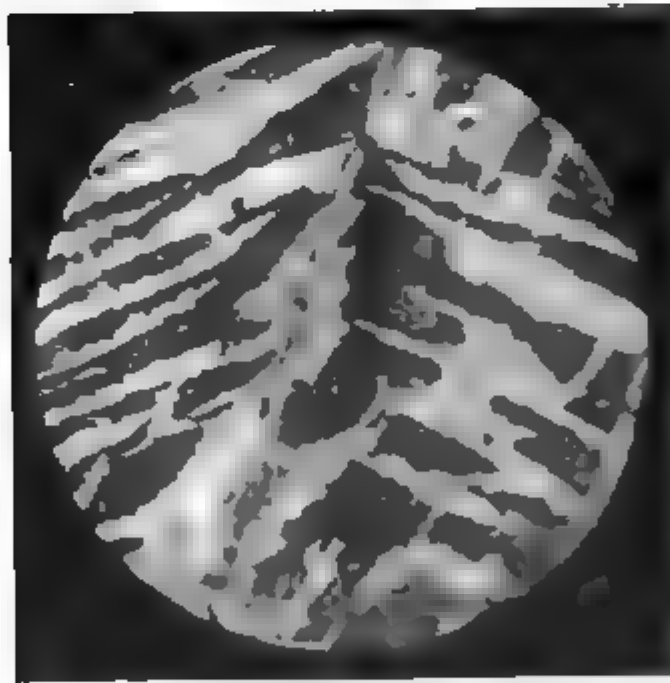


FIG. 43.—0.45 per cent. Carbon. ( $\frac{1}{4}$  in. objective.)

The brief account thus rendered of steel micrography directs attention only to the salient features of the subject. The authors are of opinion that a more complete account would be out of place in a book purporting to deal with the "Analysis of Steel-Works' Materials."

They have pleasure in appending, however, a bibliography of the subject, which constitutes a complete record of the published work

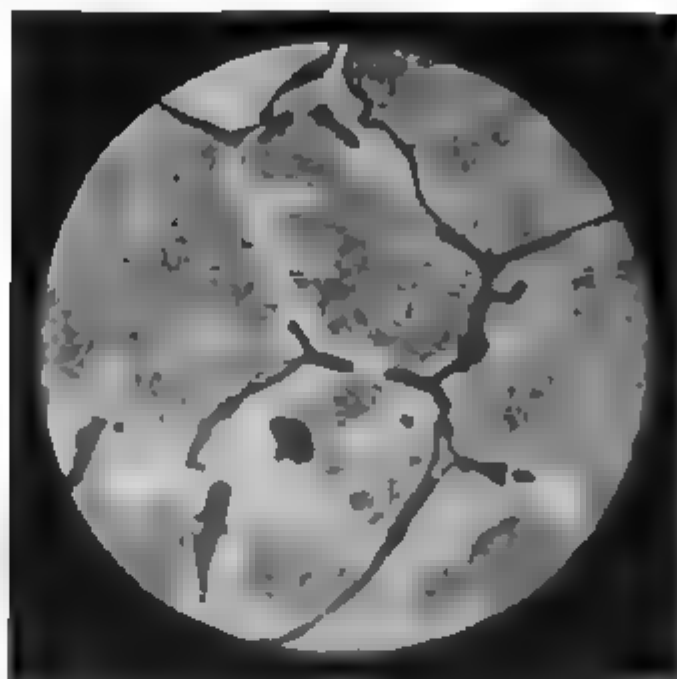


FIG. 44.—Steel Casting. Silicon, 0.3; Manganese, 0.6; Carbon, 0.4. ( $\frac{1}{2}$  in. objective.)

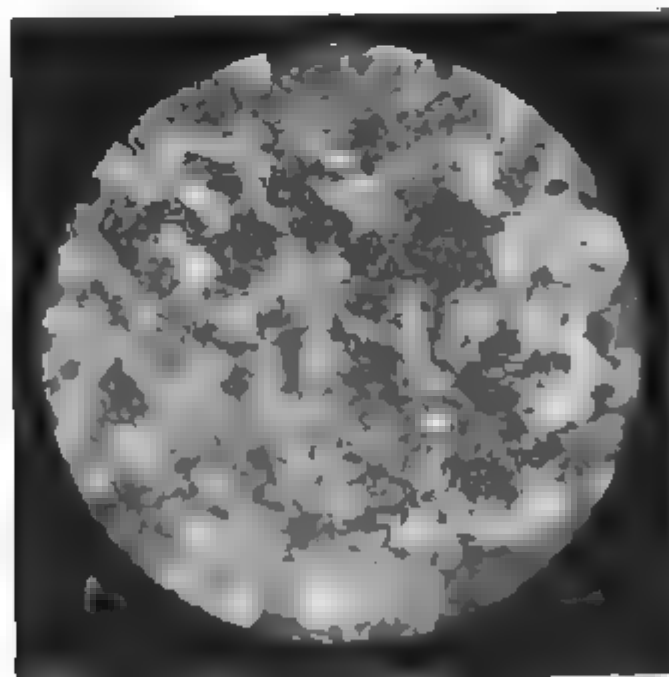


FIG. 45.—Annealed Steel Casting. ( $\frac{1}{2}$  in. objective.)

executed prior to the foundation of the *Metallographist*. In doing so they desire to thank its compiler, A. L. Colby, and the editor of the journal alluded to, for permission to reproduce it here



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The accompanying illustrations, Figs. 46 to 70, are appended for the sake of completeness. Most of them are photographed (with the  $\frac{1}{8}$ " objective) from the actual specimens.

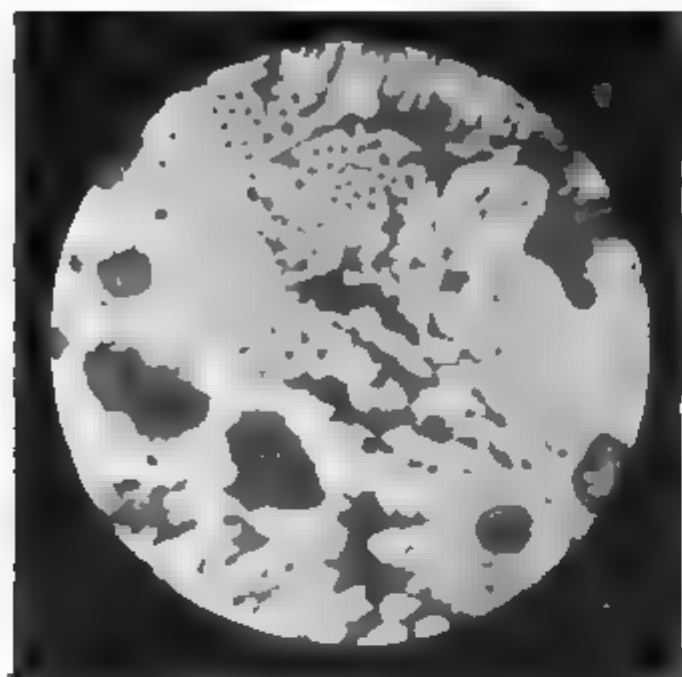


FIG. 46. Swedish White Iron.  
( $\frac{1}{8}$  inch objective.)

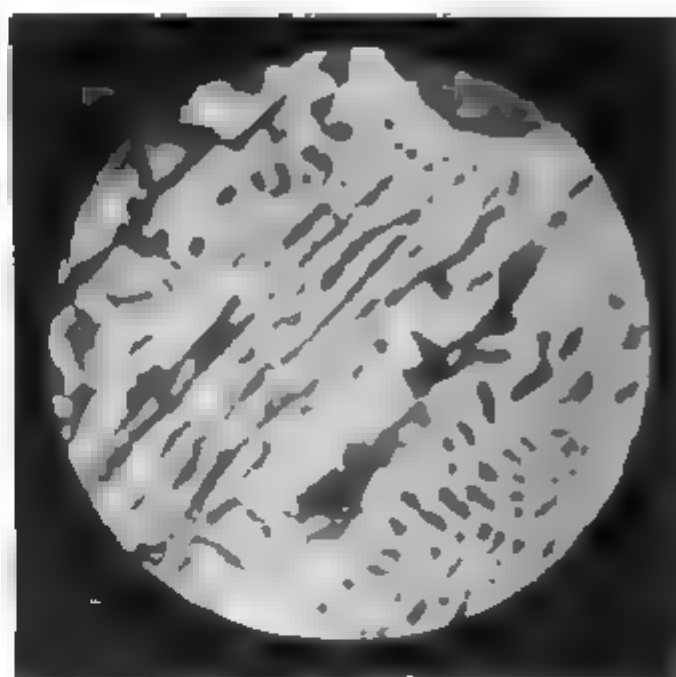


FIG. 47.—American 'Washed' Metal.  
( $\frac{1}{8}$  inch objective.)

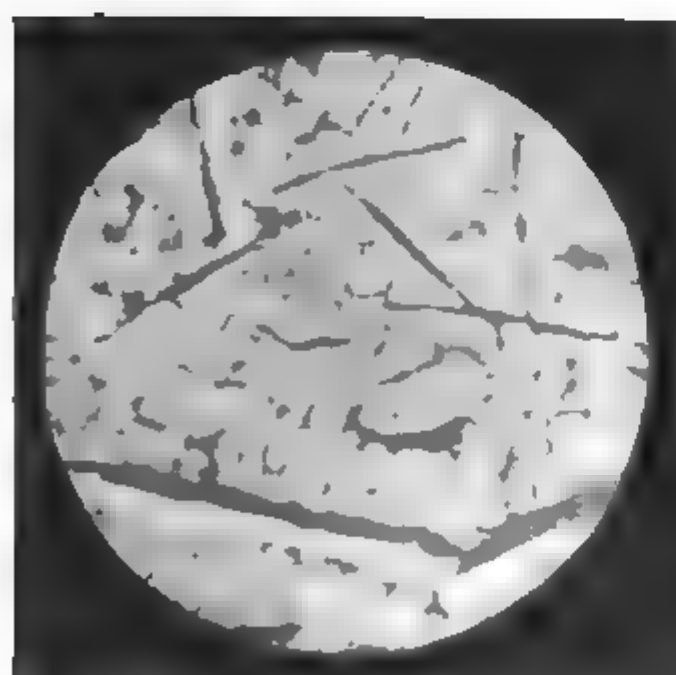


FIG. 48.—Cleveland Grey Pig Iron (Stead).  
(50 diameters.)

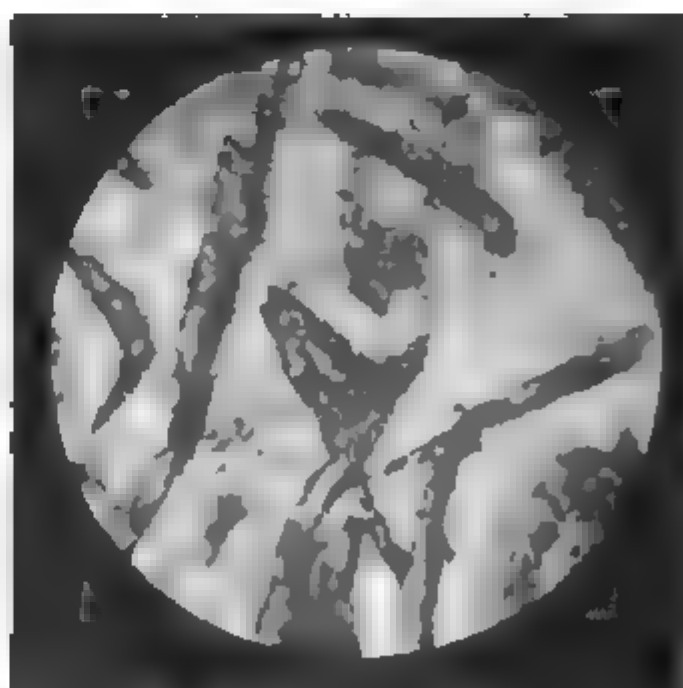


FIG. 49.—Grey Pig Iron.  
( $\frac{1}{8}$  inch objective.)

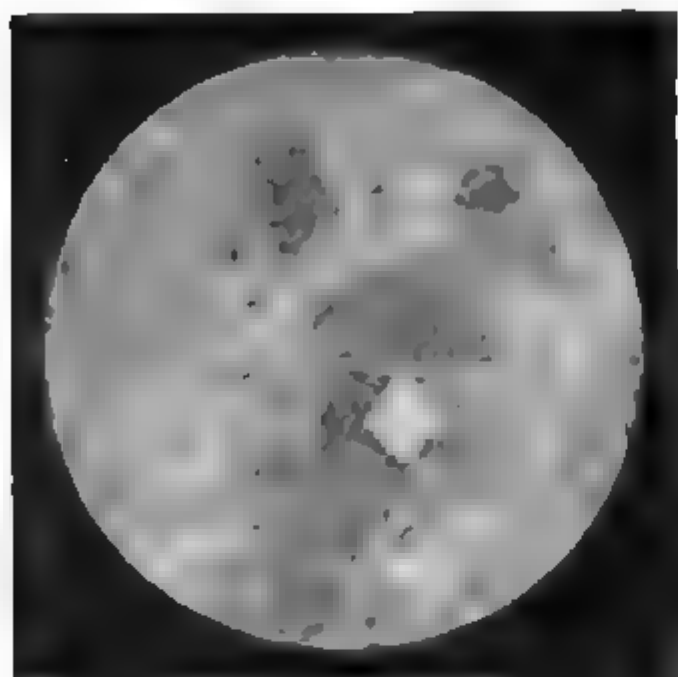


FIG. 50.—Pig Iron. (Heat-tinted, showing crystal of phosphide of iron.)  
( $\frac{1}{8}$  inch objective.)

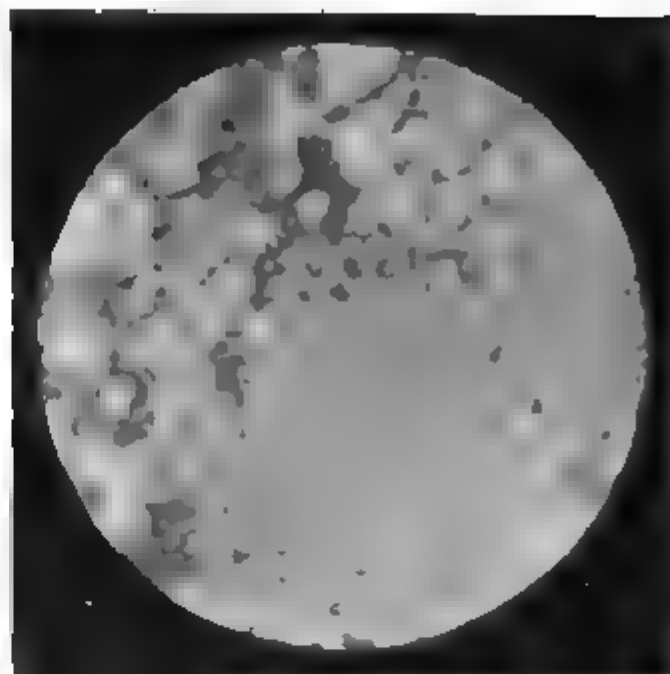


FIG. 51.—Sorby's Spiogel.  
( $\frac{1}{8}$  inch objective.)

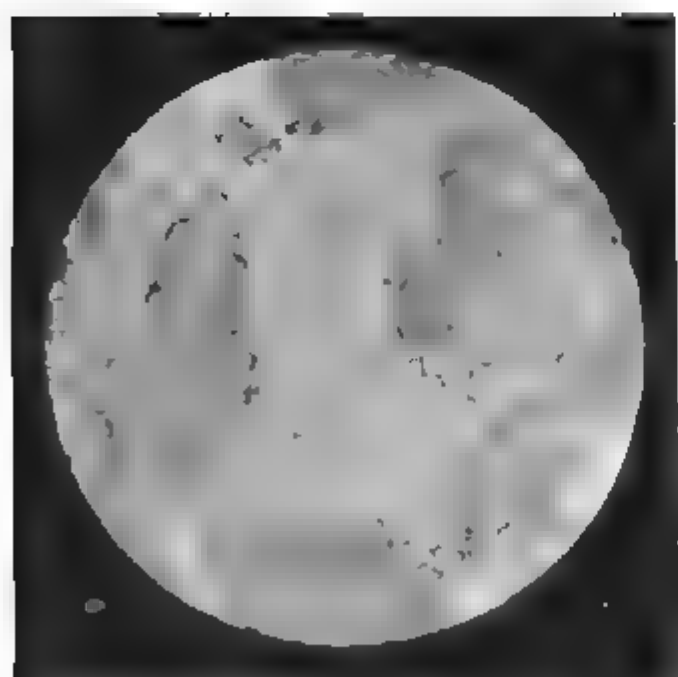


FIG. 52.—No. 2 Cemented Bar Iron. (Median layer, carbon 0.5 per cent.)  
(Unetched,  $\frac{1}{8}$  inch objective.)

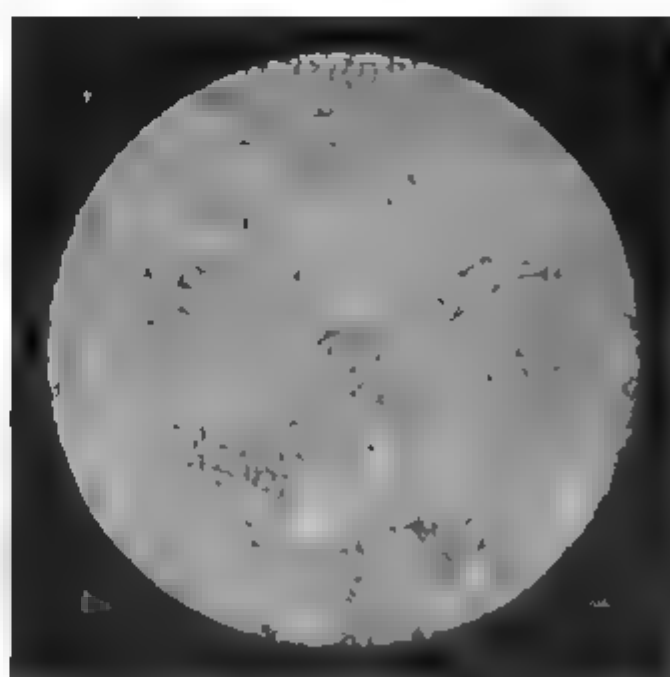


FIG. 53.—No. 2 Cemented Bar Iron. (Outer layer, carbon 0.9 per cent.)  
(Unetched,  $\frac{1}{8}$  inch objective.)

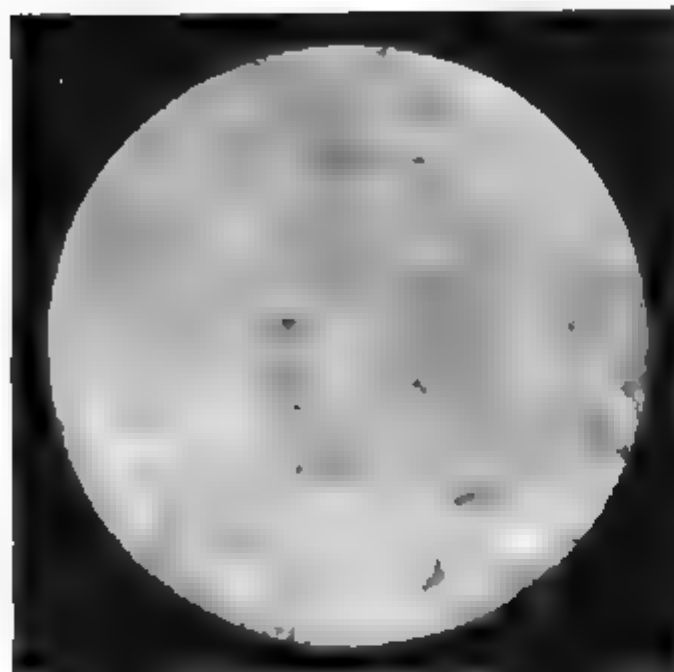


FIG. 54.—No. 3 Cemented Bar Iron. (Outer layer, carbon 1.3 per cent.) (1 inch objective.)

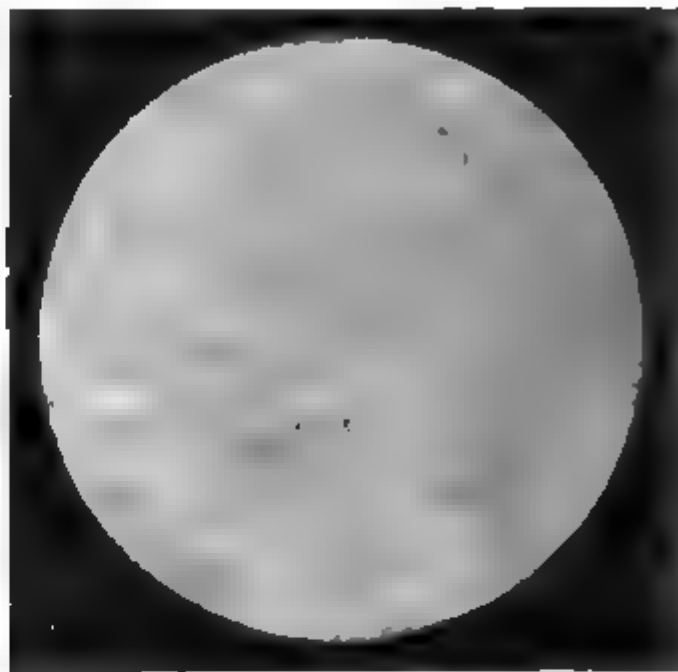


FIG. 55.—No. 3 Cemented Bar Iron. (Carbon 1.6 per cent.) (1 inch objective.)



FIG. 56.—No. 6 Cemented Bar Iron. (Carbon 1.8 per cent.) (1 inch objective.)

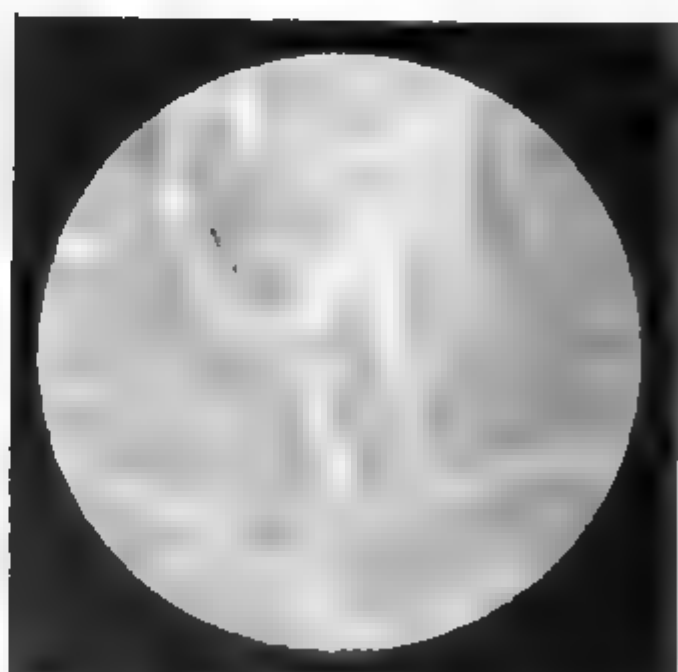


FIG. 57.—'Glazed' Bar Iron. (Carbon 1.9 per cent.) (1 inch objective.)

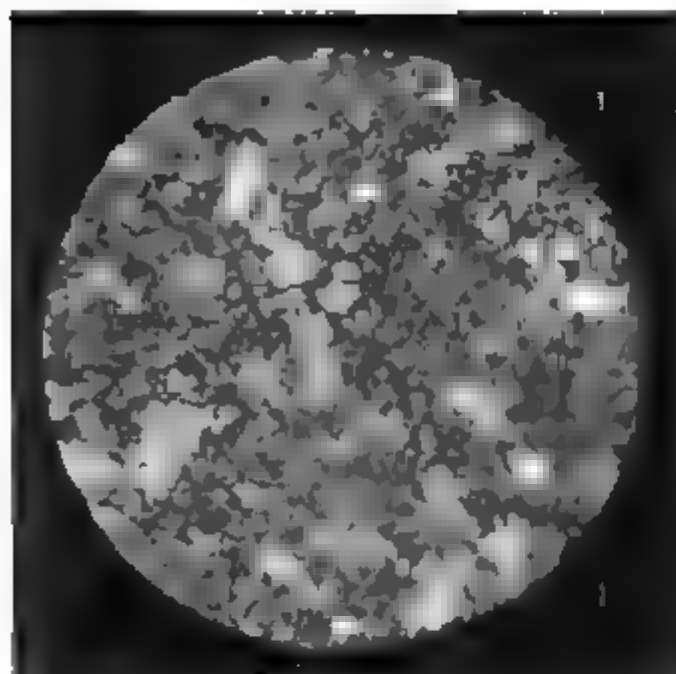


FIG. 58.—Self-hard Steel.  
( $\frac{1}{4}$  inch objective.)

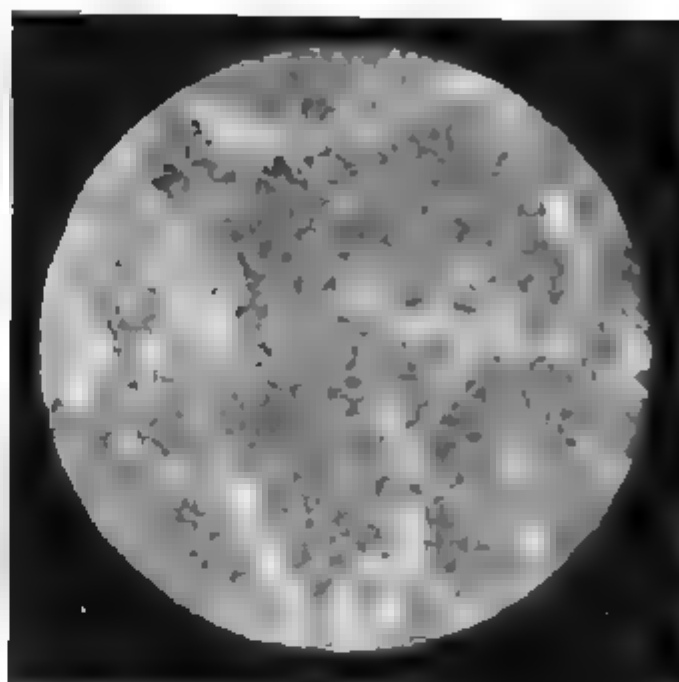


FIG. 59.—Tempered Gun Steel.  
( $\frac{1}{4}$  inch objective.)

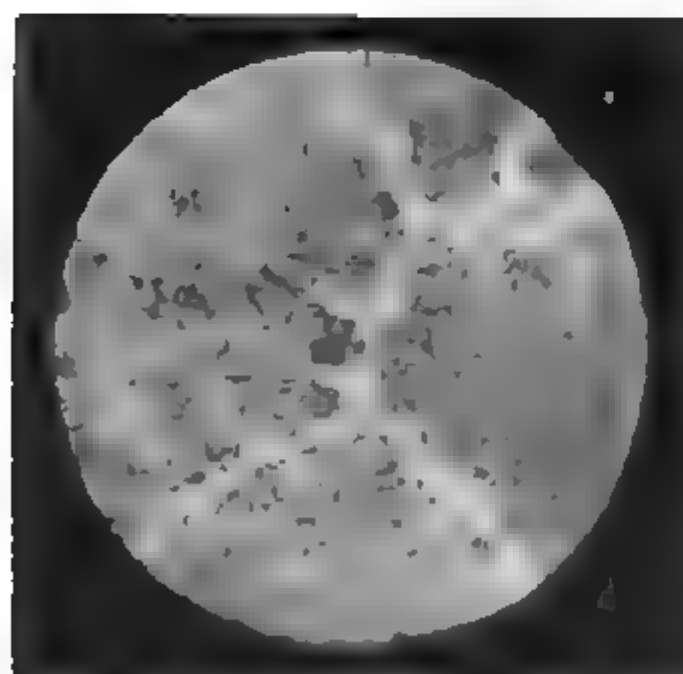


FIG. 60.—Annealed Steel. (Carbon 1.7 per cent.)  
( $\frac{1}{8}$  inch objective.)

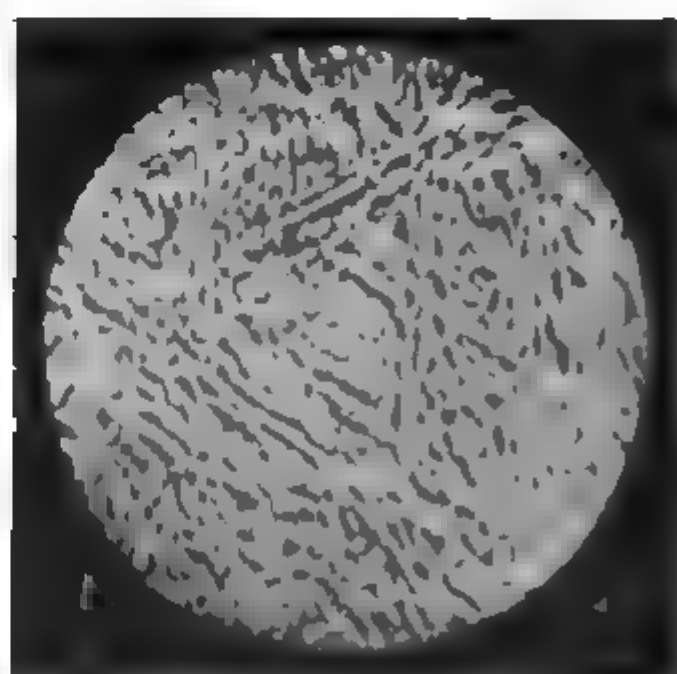


FIG. 61.—Martensite (Osmond)  
(1000 diameters.)

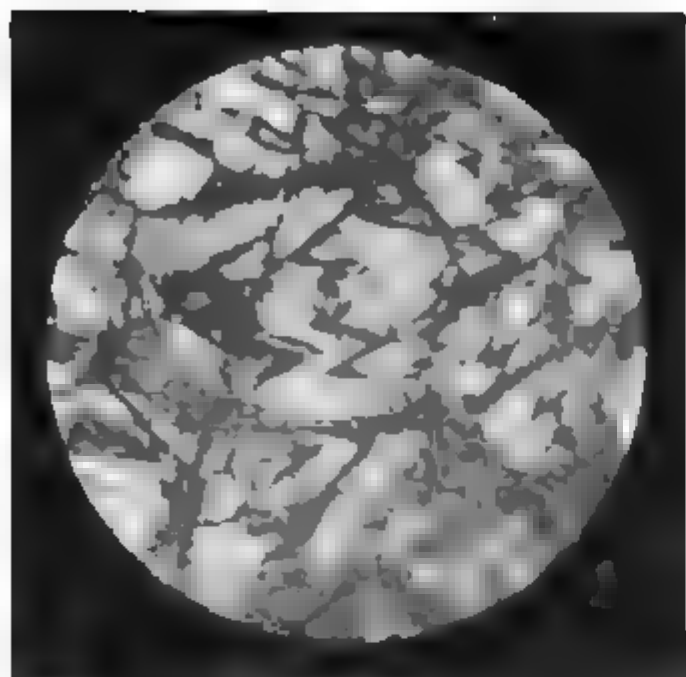


FIG. 62.—'Austenite.'  
( $\frac{1}{4}$  inch objective.)

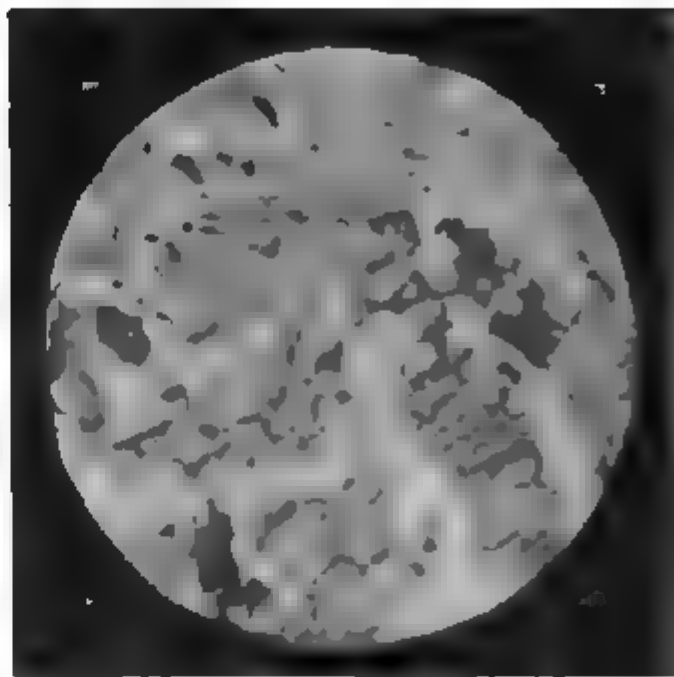


FIG. 63.—33 per cent. Ferro-Vanadium.  
( $\frac{1}{4}$  inch objective.)

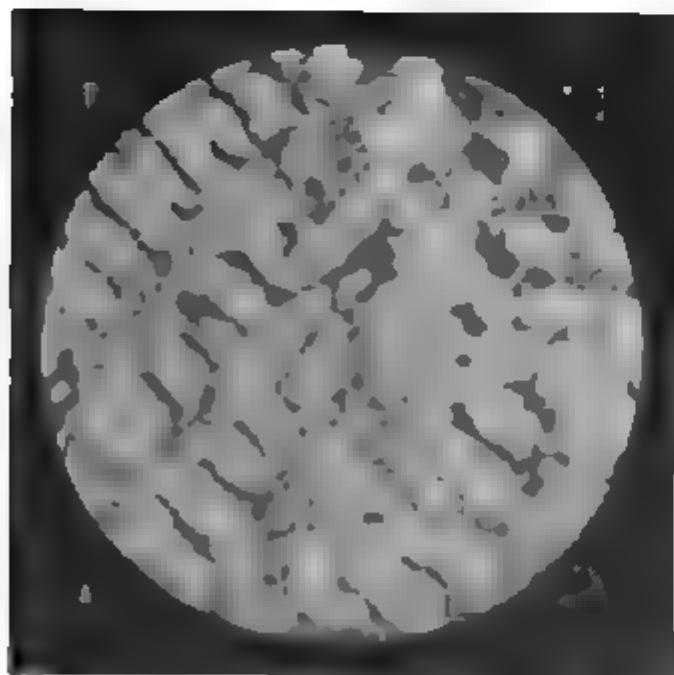


FIG. 64.—43 per cent. Ferro-Vanadium.  
( $\frac{1}{4}$  inch objective.)

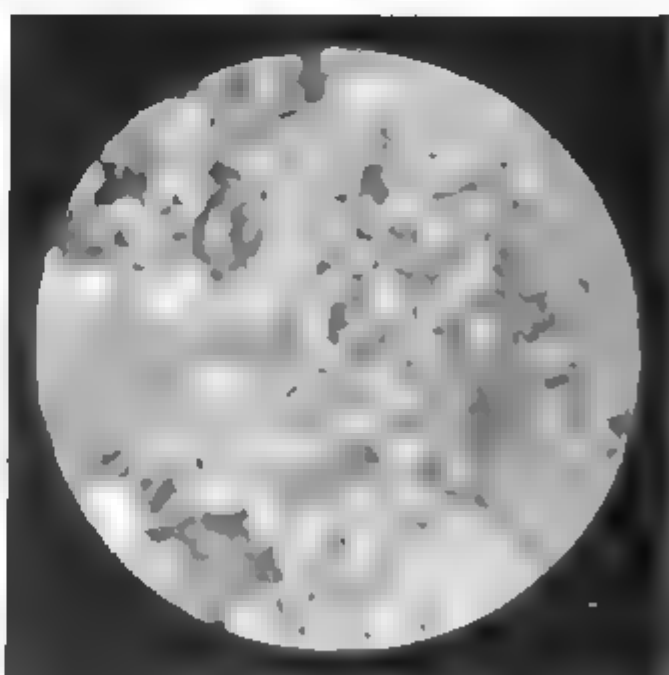


FIG. 65.—28 per cent. Ferro-Titanium.  
( $\frac{1}{4}$  inch objective.)



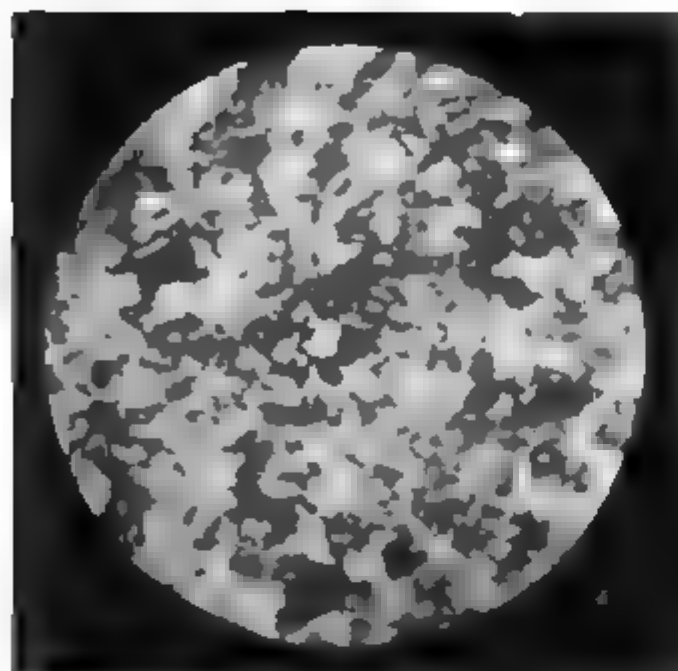


FIG. 66.—Ferro-Molybdenum. (Mo=25 per cent., carbon 0.38 per cent.)  
( $\frac{1}{4}$  inch objective.)

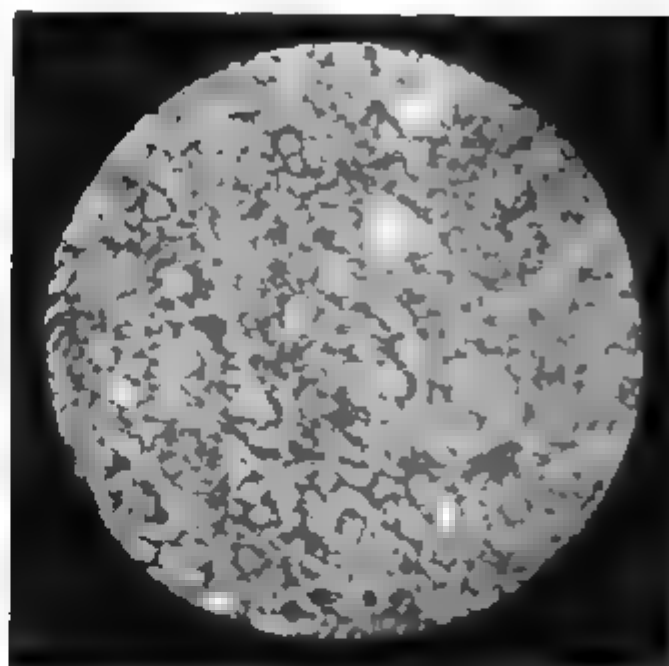


FIG. 67.—'Self-hard' Alloy. (Tungsten, 50.7; chromium, 8.52; carbon, 2.56 per cent.)  
( $\frac{1}{4}$  inch objective.)

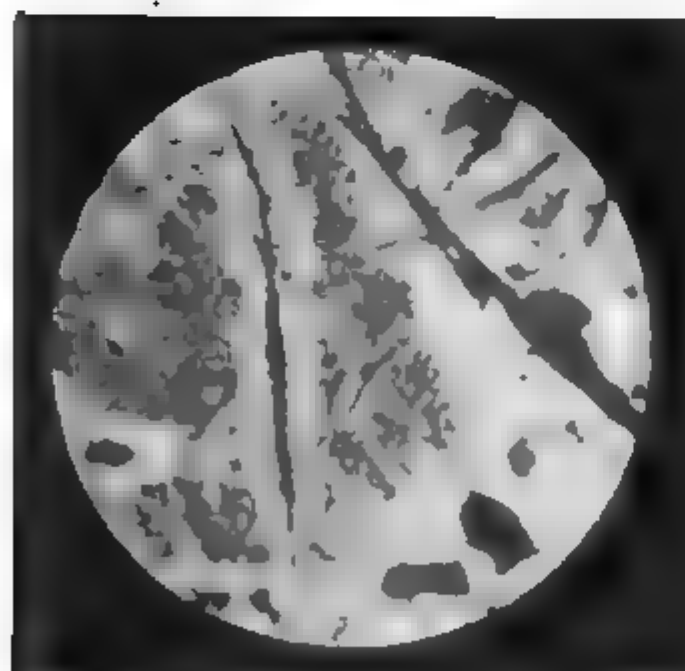


FIG. 68.—10 per cent. Ferro-Silicon.  
(Unetched,  $\frac{1}{4}$  inch objective.)

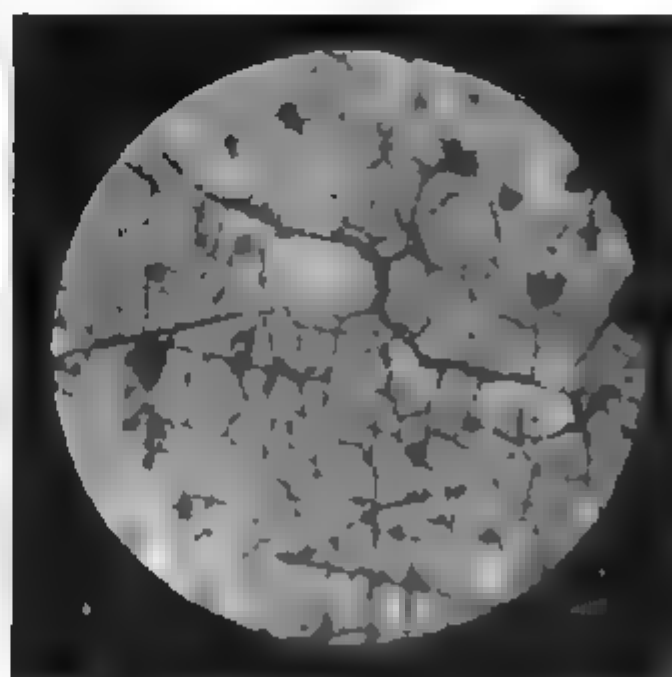


FIG. 69.—Alloy of Pure Iron, with 10 per cent. of silicon, made in steel-melting crucible.  
( $\frac{1}{4}$  inch objective.)

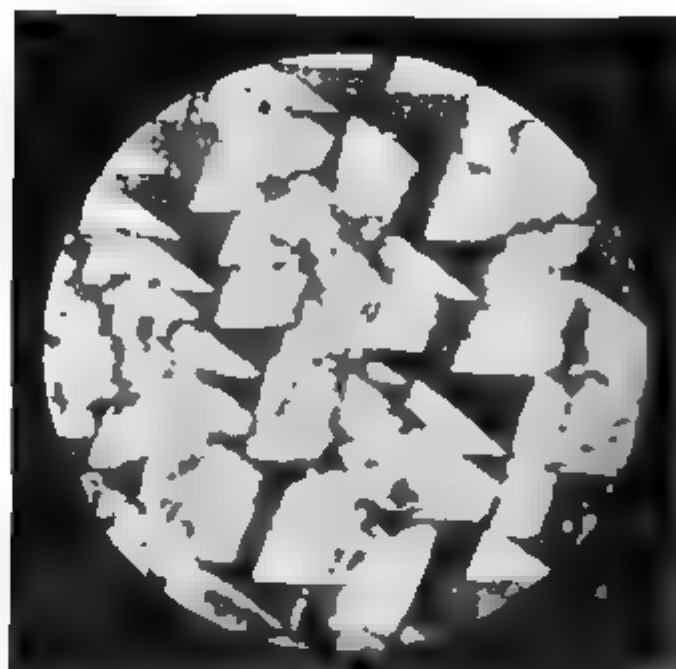


FIG. 70.—25 per cent. Ferro-Silicon.  
(Etched with strong hydrochloric acid.  $\frac{1}{2}$  inch objective.)

## PART XII. PYROMETRY.

THE heat treatment of metals in general, and of steel in particular, has become a very important matter, so that a brief account of the method of manipulating the Le Chatelier Pyrometer is introduced in this book for the assistance of the increasing number of steel-works' chemists who are being called upon to handle it. The recent publication of Le Chatelier's book on *High Temperature Measurements* renders it unnecessary to deal with the subject of pyrometry exhaustively.

To intelligently apply the Le Chatelier and similar pyrometers, under varying conditions, it is necessary to keep in mind the principles underlying their use. When two dissimilar metals are joined together so as to form a complete circuit, there must be two junctions. If one of the junctions be made hotter than the other a current of electricity passes round the circuit, and, with the same couple and circuit, for each difference in temperature there is a definite strength of current generated. In the Le Chatelier pyrometer a couple is used in which the dissimilar metals are platinum and platinum alloyed with ten per cent. of rhodium. The current produced by known differences of temperature is passed through a d'Arsonval dead-beat galvanometer and the deflection of the galvanometer mirror in each case is noted in the usual way from the movement of a spot of light on a millimetre scale. By taking these observations through the required range of temperature and drawing a fair curve through the points obtained, plotting temperatures as ordinates and the corresponding actual movement of the spot of light on the scale in millimetres as abscissae, a calibration curve is made from which an unknown difference of temperature between the hot and the cold junction may be read off from the deflection given, and hence, the temperature of the cold junction being known, the actual temperature of the hot junction is determined by addition. Again, to bring

the hot junction to a given temperature it is obviously only necessary to find from the curve the millimetres corresponding to the required temperature less the temperature of the cold junction, and the result is the actual distance the spot of light must move from the zero for the hot junction to be at the required temperature. These are practically the only three types of problem that occur, namely, calibrating the instrument, finding an unknown temperature, and bringing the hot junction to a required temperature.

If it were necessary to have the galvanometer in the platinum and platinum-rhodium circuit the usefulness of the instrument would be

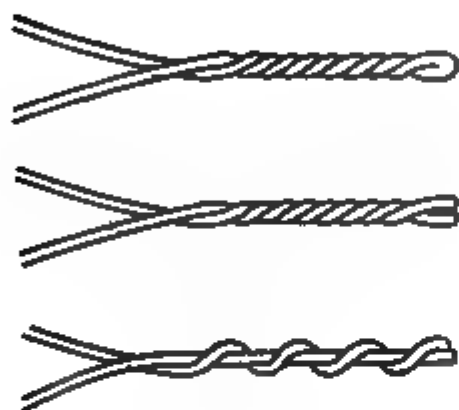


FIG. 71.

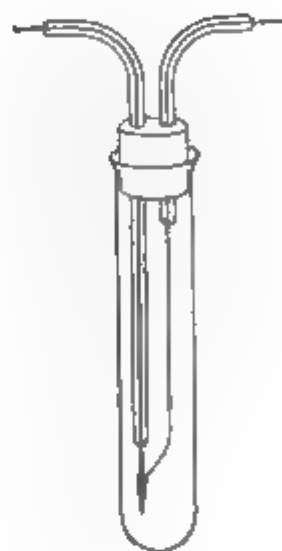


FIG. 72.

much curtailed. It is found, however, both theoretically and practically, that if the ends of the wires forming the cold junction, instead of being joined together, be each soldered to a copper wire, these two junctions kept at the same temperature, and the circuit completed, the two junctions become the cold junction, and then sufficient copper wire may be employed to form leading lines from any required number of furnaces to one galvanometer, which, by the aid of a switch, may be used for any of these furnaces in turn without the observer's leaving his place. To form the hot junction the wires need not be either fused or soldered together, but only closely twisted round each other, not one round the other, as in this way they are apt to come apart on heating. This point must be carefully watched, as the platinum-rhodium wire being stronger than the pure platinum there is a tendency for the latter to twist round the former, and this tendency should be counteracted by handicapping the platinum-rhodium wire, bending it back before each twist is made. Two, or at most three, twists will generally be found sufficient. This is the most convenient method for experi-

mental purposes, but where a couple is fixed in a furnace and left for prolonged periods it is safer to just fuse the ends of the wires together by placing them for an instant in an oxy-hydrogen flame (see Fig. 71).

The wires should be protected from contact with metals which would alloy with the platinum and from such substances as fused magnetic oxide of iron or carbonaceous matter, which render them brittle.

Where a considerable degree of accuracy is required the cold junction is conveniently kept in water in a glazed earthenware vessel with a lid made of sheet lead. A large hole is cut in the centre of this lid for the thermometer for convenience in stirring before taking the cold junction temperature; three small holes for  $6'' \times \frac{1}{2}''$  test tubes, in two of which are the soldered junctions of the copper wires with the platinum and platinum-rhodium wires respectively (the solder being preserved from disintegration by half filling the test tubes with alcohol); the third to keep the hot junction dry when taking the zero of the instrument, and to prevent possible breakage of the protecting glass tubes during subsequent calibration or similar work (Fig. 72).

For ordinary furnace work the cold junction is contained in a hinged wooden case and the temperature of the surrounding air may be taken as that of the cold junction (Fig. 73).

The diagram Fig. 74 indicates how the temperatures of two and similarly several furnaces may be read in turn on the same scale with only one galvanometer.  $H1$  and  $H2$  are the hot junctions,  $C1$  and  $C2$  the cold junctions. A wire joins the + or platinum-rhodium terminal of the galvanometer to the centre  $D$  of a

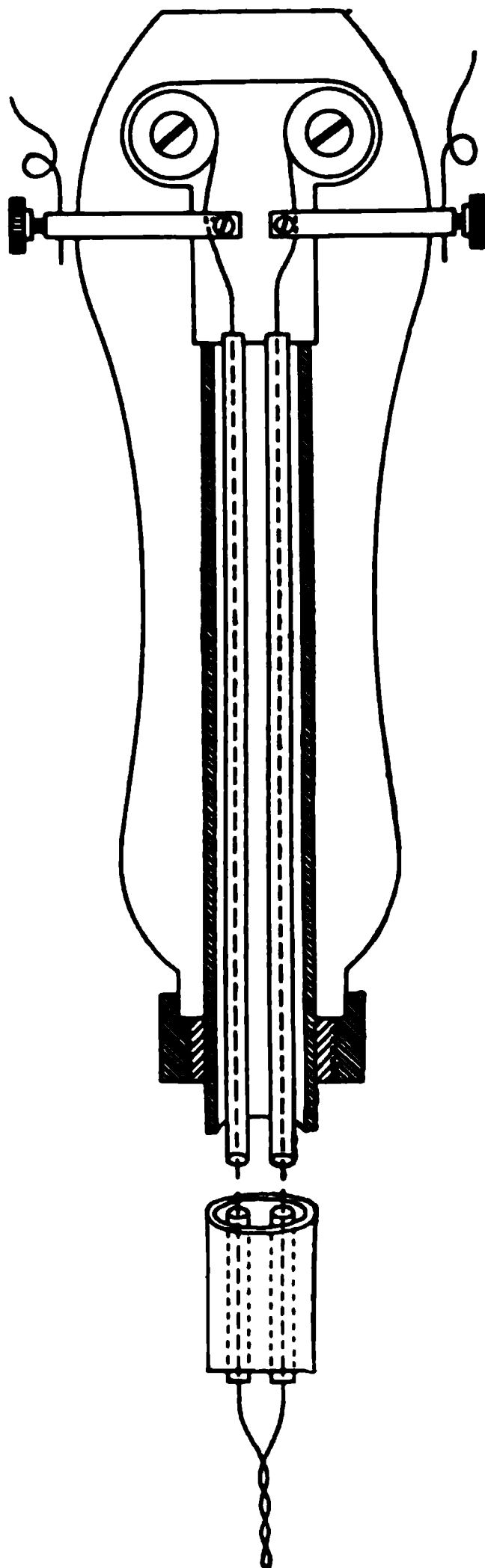


FIG. 73.

switch board *B* placed under the scale *S*. The movable contact arm *DO* is in electric contact with the centre, and brass pieces 1, 2, etc., are insulated from *D* and from one another, but joined to their respective wires from furnaces 1, 2, etc. A common wire is carried from the — or platinum terminal of the galvanometer and is connected to the — terminals throughout the system. The direction of the current is from the *Pt* to the *Pt-Rd* through the hot junction. It will be seen by following the wires round the only possible circuit that if the arm *DO* be turned to No. 1 the reading will be that of No. 1 furnace; if to No. 2, of No. 2 furnace, and so on.

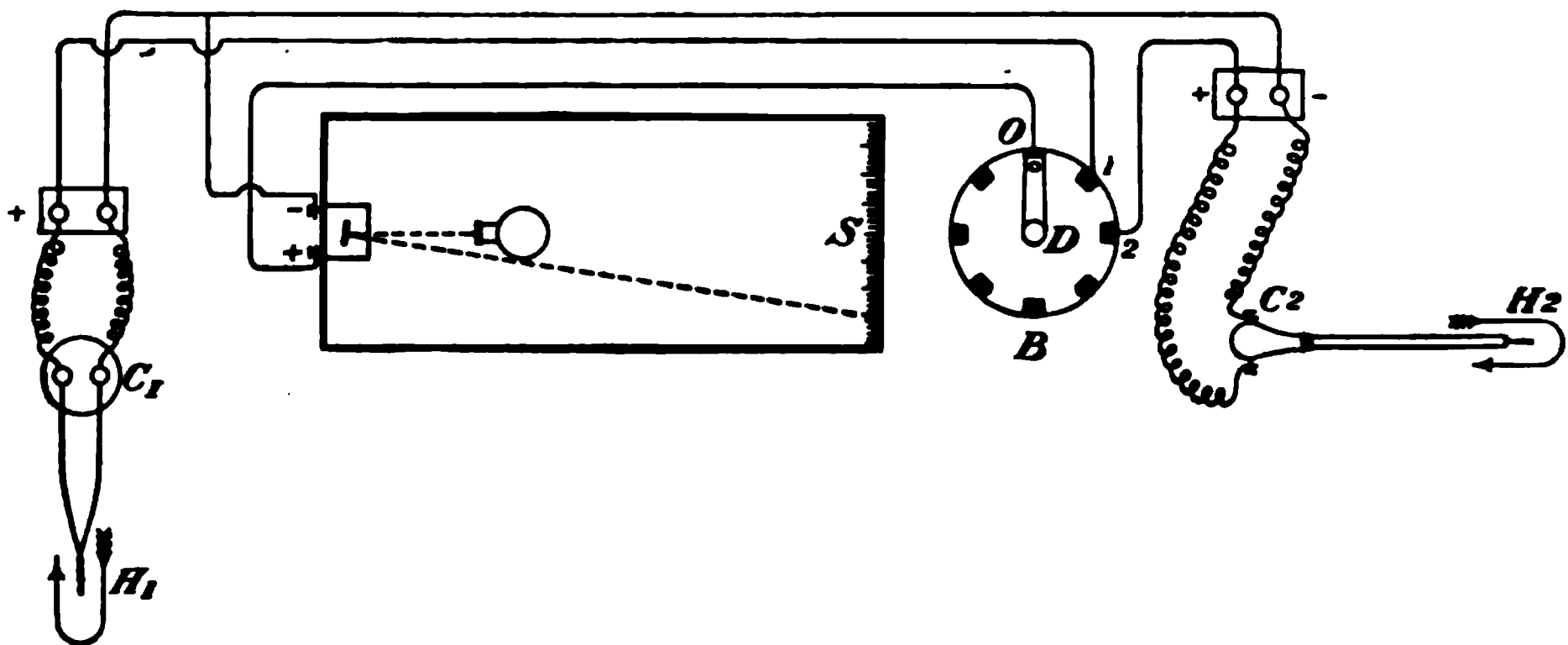


FIG. 74.

### Calibration of the Pyrometer.

As the calibration 'curve' is found to be practically a straight line above about  $550^{\circ}\text{C.}$ , it is generally quite sufficient to use as standards the melting points of tin ( $232^{\circ}\text{C.}$ ), lead ( $327^{\circ}\text{C.}$ ), and potassium sulphate ( $1015^{\circ}\text{C.}$ ), and the boiling points of water ( $100^{\circ}\text{C.}$ ), sulphur ( $445^{\circ}\text{C.}$ ), and selenium ( $665^{\circ}\text{C.}$ ).

The zero of the instrument is noted by bringing the two junctions to the same temperature, generally by placing the hot junction in a dry test tube in the water containing the cold junction, or in the case of the wooden-cased cold junction by leaving the instrument in the air in such a position that the two junctions will reach as nearly as possible the same temperature, and taking the reading on the scale when constant. In all experiments it is necessary to arrange that the wires shall not touch except at the hot junction, and they must therefore always be suitably insulated, as by running one or both through quill glass tubing, thin pipe stems, or two-hole pipe-clay tubing manufactured

for the purpose. The reading for boiling water can be taken with an ordinary wash bottle, the jet tube being replaced by a closed glass tube and the water allowed to boil till the reading is constant, as in all the other boiling-point determinations. For lead and tin, small fireclay crucibles holding a few ounces are used, and, after melting the metal over a bunsen and inserting the couple, protected by a closed hard glass tube, into the molten metal, the flame is removed, and the spot of light on the scale watched. It generally rises a few millimetres owing to the heat in the bottom of the crucible, then turns and begins to fall steadily, becomes stationary when the metal begins to solidify, remains so till all the metal is solid, and then begins to move steadily down again. The exact point is thus easily determined. Similarly, the point for potassium sulphate is obtained, only a platinum crucible is used, the wires are bare, and the oxy-hydrogen flame is required for melting the salt. The sulphur point is best done in a small registered pattern flask, with an asbestos jacket extending from the level of the liquid to the top of the flask, a bunsen burner being the most suitable source of heat, and the selenium in a hard-glass test tube similarly covered, and using an ordinary foot blowpipe. In the last two cases, for a stopper the protecting tube and two open tubes are packed in the mouth of the vessel with asbestos, which is soon bound into a solid mass by the condensation of vapour among the fibres.

Example of Calibration.

Zero, - - - - -	14.5 mm.	Cold Junction,	18° C.
Boiling Water, - - - - -	29.0	Temperature,	100°
	<u>14.5</u>		<u>82°</u>
Zero, - - - - -	14.5	Cold Junction,	18°
Tin (solidifying), - - - - -	56.5	Temperature,	232°
	<u>42.0</u>		<u>214°</u>
Zero, - - - - -	14.5	Cold Junction,	18°
Lead (solidifying), - - - - -	79.0	Temperature,	327°
	<u>64.5</u>		<u>309°</u>
Zero, - - - - -	14.5	Cold Junction,	19°
Sulphur (boiling), - - - - -	109.0	Temperature,	445°
	<u>94.5</u>		<u>426°</u>
Zero, - - - - -	14.5	Cold Junction,	19°
Selenium (boiling), - - - - -	172.0	Temperature,	665°
	<u>157.5</u>		<u>646°</u>

Zero,  $\frac{21.0}{291.0}$   
 Potassium Sulphate (solidifying),  
270.0 mm.

Cold Junction,  $\frac{15^\circ}{1015^\circ}$   
 Temperature,  
1000° C.

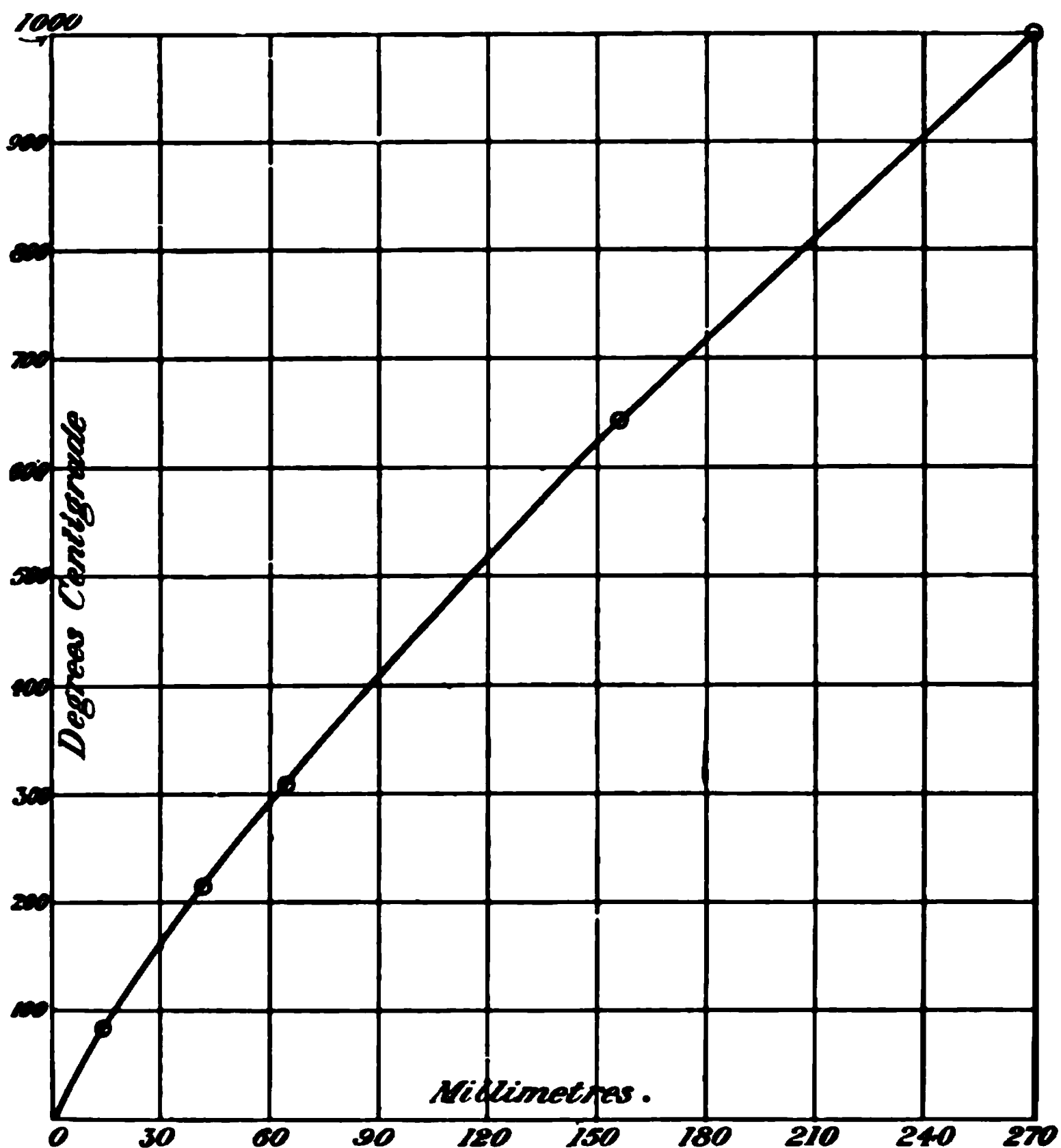


FIG. 75.—Calibration Curve. ("C." couple; March, 1902.)

### Typical Problems.

1. "The recalescence of a 0.9 per cent. carbon steel on cooling was found to take place at 181 mm. on the scale, the temperature of the cold junction being  $15^\circ\text{C.}$ , and the zero of the instrument 17 mm.; at what temperature was the recalescence exhibited?"

181 mm. - 17 mm. = 164 mm., corresponding to a temperature of  $665^\circ\text{C.}$  Then  $665^\circ + 15^\circ = 680^\circ\text{C.}$ , the required temperature.



2. "The zero and cold junction being the same as in problem 1, what should the scale reading be in order to indicate a temperature of 950° C., at which it is required to maintain the annealing furnace for so many hours?"

$950^{\circ} - 15^{\circ} = 935^{\circ} \text{ C.}$ , corresponding to a scale reading of 250 mm.,  
and  $250 \text{ mm.} + 17 \text{ mm.} = 267 \text{ mm.}$ , the required reading.

### Recording Observations.

The critical points in the heating or cooling of metals or alloys are most clearly shown by noting the number of seconds the spot of light takes to pass each millimetre on the scale, the hot junction being carefully fixed in a suitable receptacle in the piece of metal to be examined. This may be done by two observers, one watching the scale and the other a centre seconds watch, the observer at the scale

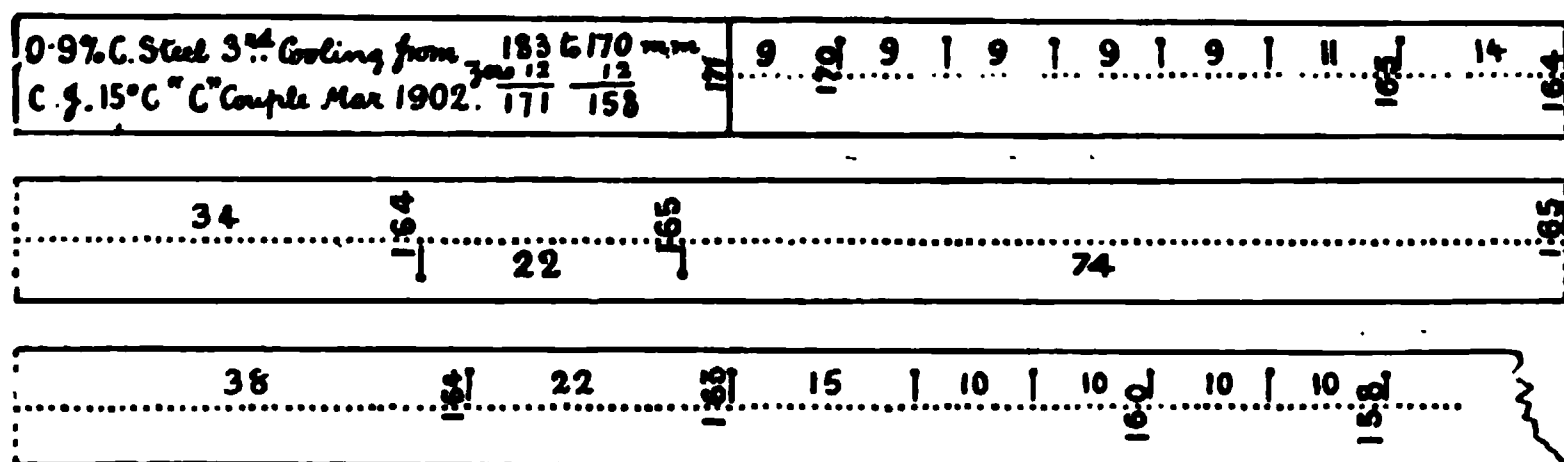


FIG. 76.

calling out as each millimetre mark is reached, and the other noting the number of seconds between each call. The record is more easily made by one observer with the aid of a chronographic recorder marking seconds continuously on a tape throughout the experiment, and fitted with two electric signals, marking at will one on each side of the seconds' marks on the same tape. One of these signals is used for the passing of a millimetre in falling and the other in rising. This tape, marked with the name or number of the sample, the scale readings for the start and finish of the recording, the zero of the instrument, the temperature of the cold junction, and a means of identifying the proper calibration curve to use, contains all the necessary information for plotting the curves and studying the critical points, if any, of the metal or alloy, as shown in Fig. 76.

Cooling of Plumber's Solder (2 of Lead to 1 of Tin), from 49 mm. to 24 mm. C. J. 17° C. Dead stop at 31 mm.						Cooling of 0.9 per cent. Carbon Steel from 171 to 158 mm. C. J. 15° C.		
mm.	Secs. per mm.	Total Secs.	mm.	Secs. per mm.	Total Secs.	mm.	Secs. per mm.	Total Secs.
49	0	0	34	25	313	171	0	0
48	11	11	33	23	336	170	9	9
47	11	22	32	21	357	169	9	18
46	11	33	31	31	388	168	9	27
45	14	47	31	44	432	167	9	36
44	31	78	32	35	467	166	9	45
43	30	108	32	81	548	165	11	56
42	30	138	31	72	620	164	14	70
41	23	161	30	14	634	164	34	104
40	22	183	29	17	651	165	22	126
39	21	204	28	16	667	165	74	200
38	22	226	27	20	687	164	38	238
37	21	247	26	20	707	163	22	260
36	21	268	25	23	730	162	15	275
35	20	288	24	25	755	161	10	285
						160	10	295
						159	10	305
						158	10	315

The zero is deducted from the scale readings before entering in the record book.

The number of millimetres passed in a minute would represent the rate of fall in temperature, hence the number of seconds taken to pass a millimetre is the inverse of a rate and the curve formed by plotting millimetres (representing temperatures), and seconds per millimetre is called an inverse rate curve. This curve shows best the slightest change in rate of heating or cooling which might pass unnoticed in the ordinary time-temperature curve. While the metal acts as an ordinary cooling body the inverse rate curve is a slowly and evenly rising line, but if any change takes place within the metal with evolution of heat, as at the carbon change point in cooling steel or during the solidification of the eutectic in plumber's solder, then the curve rises abruptly, but resumes its original direction when the action is complete. It need hardly be mentioned that the cooling sample must be shielded from draughts or other external causes which would tend of themselves to change the rate of cooling, and similarly a sample being heated must be subject to a constant source of heat (a much more difficult problem), and hence the cooling curve is chosen whenever it will serve the purpose.

The ordinary time-temperature curve, plotted with time in seconds and millimetres or temperatures as coordinates, shows if any actual rise or fall has taken place, and is the curve given by the Roberts-Austen

recording pyrometer. This is a Le Chatelier pyrometer with an automatic photographic recorder attached to keep a continuous record of the temperature of a furnace during twenty-four hours. The spot of

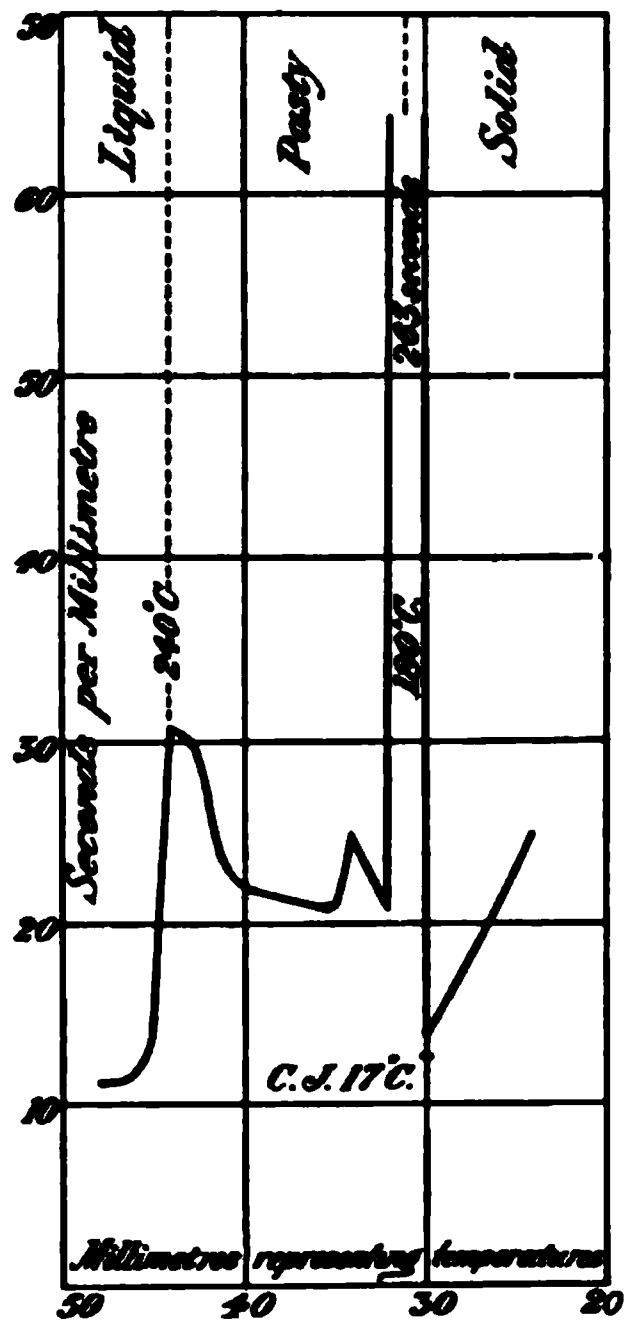


FIG. 77.—Inverse-Rate Curve of Plumber's Solder.

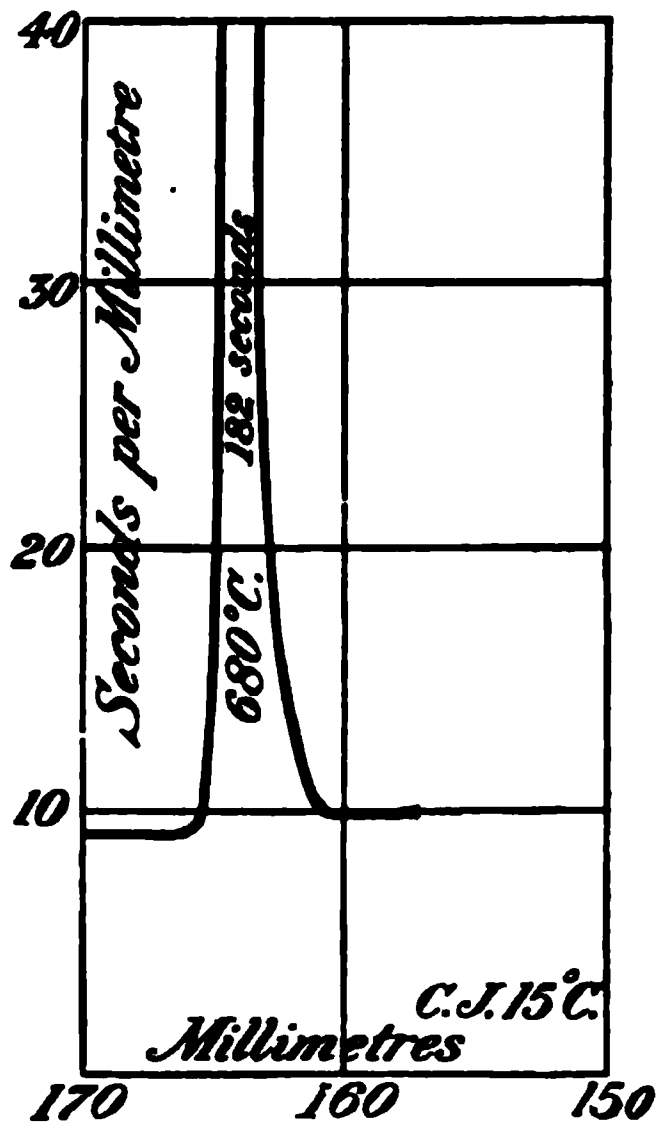


FIG. 78.—Inverse-Rate Cooling Curve of 0.9 per cent. Carbon Steel.

light leaves its record on a piece of bromide paper stretched on a drum and revolved by clockwork, the bromide paper being taken off and afterwards developed in the usual way.

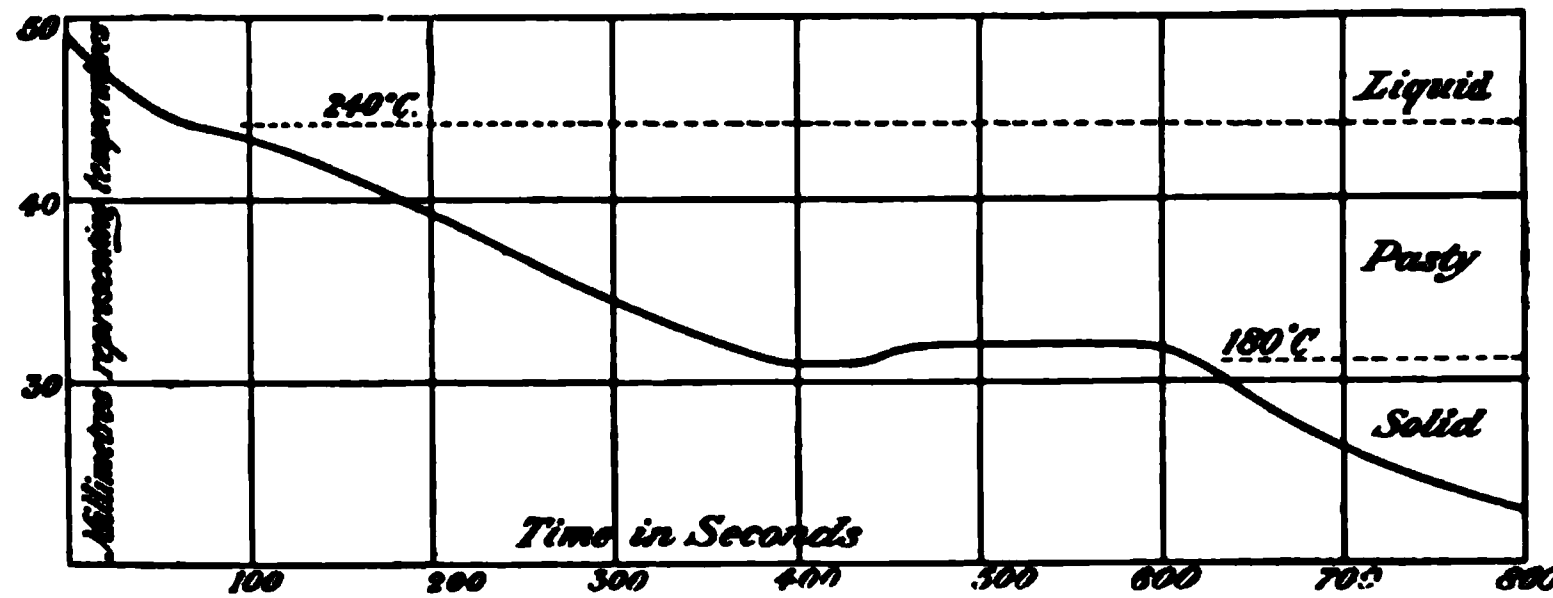


FIG. 79.—Time-Temperature Curve of Plumber's Solder.

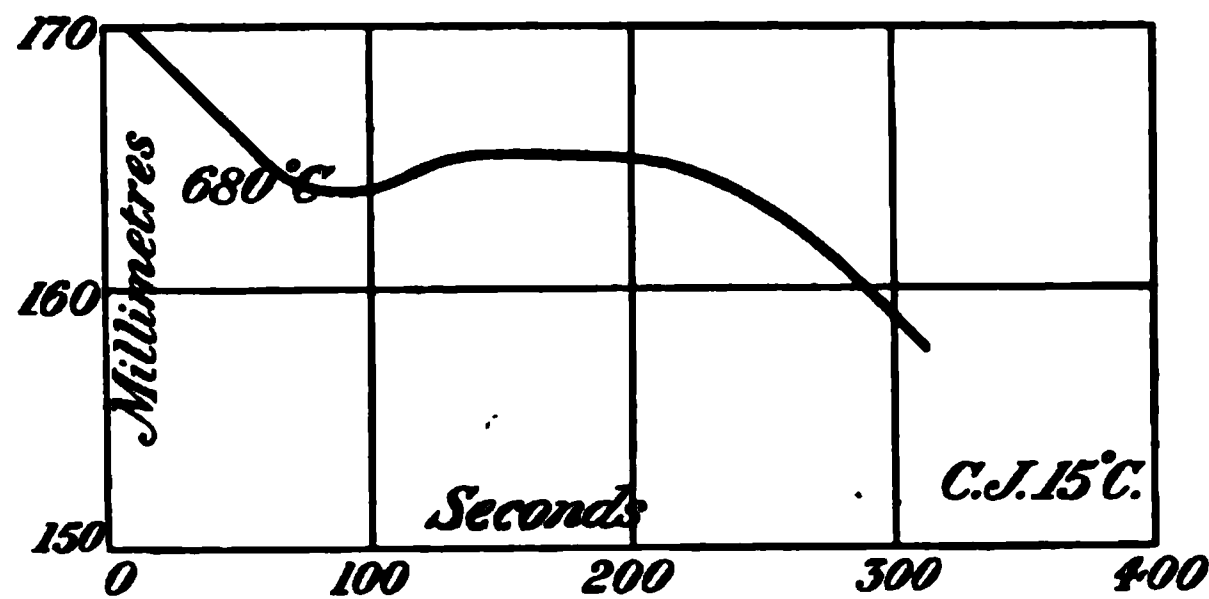


FIG. 80.—Time-Temperature Curve of 0.9 per cent. Carbon Steel.

The two appended figures (81 and 82) represent the cooling curves of steels containing 0.4 and 1.3 per cent. of carbon respectively

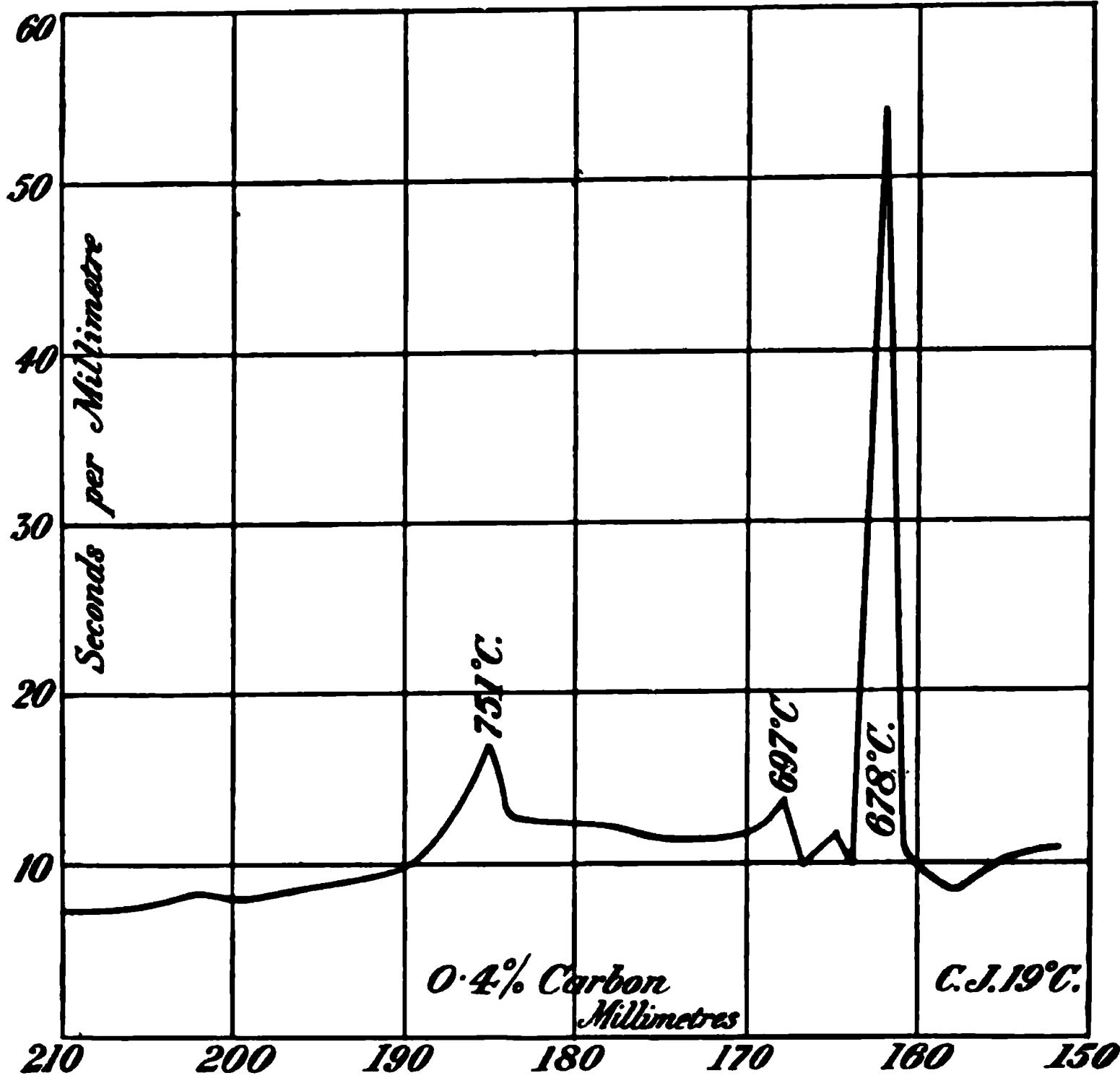


FIG. 81.

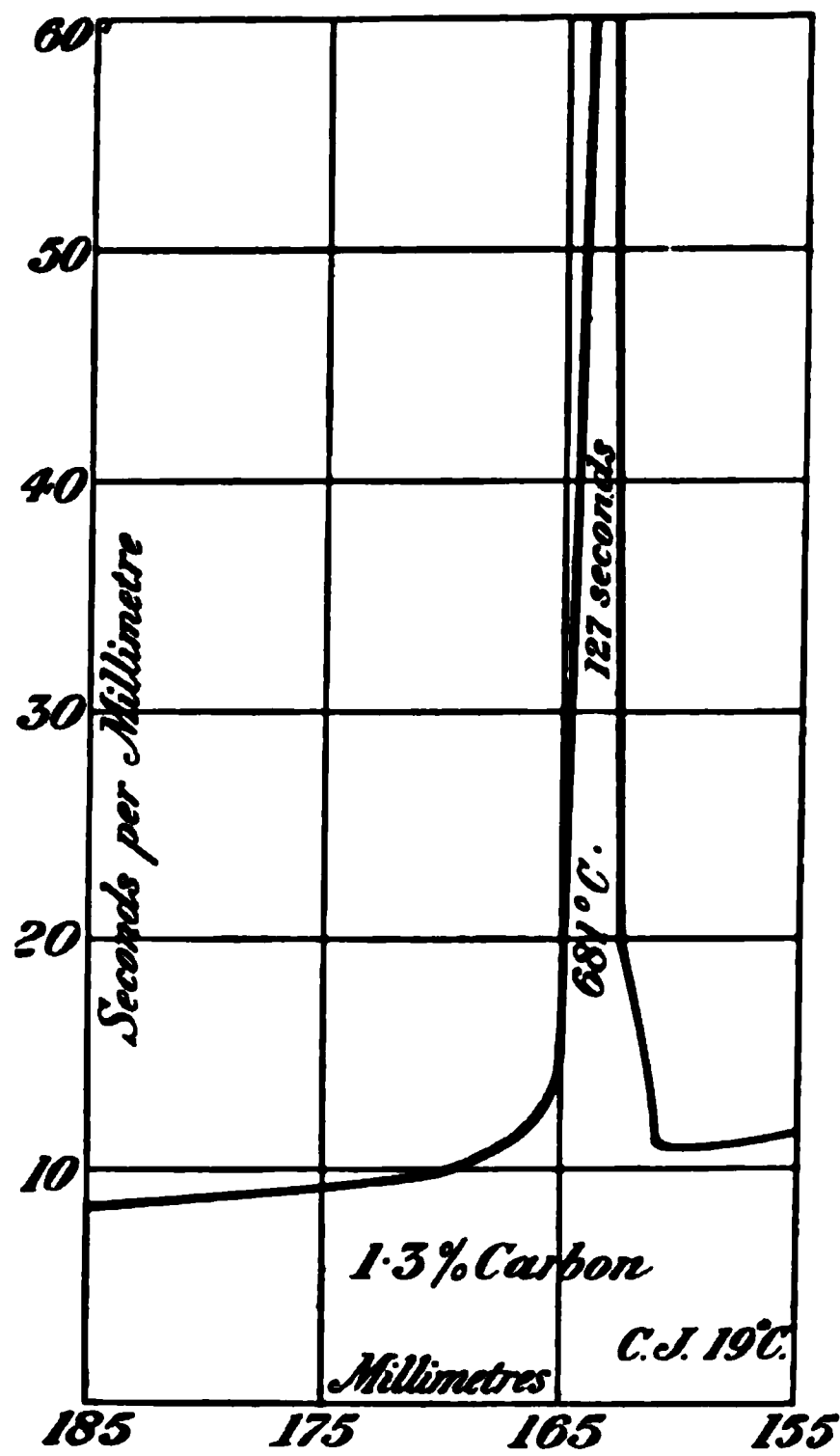


FIG. 82.

## PART XIII. MISCELLANEOUS NOTES.

### 1. Speed and Efficiency of Carbon Combustion.

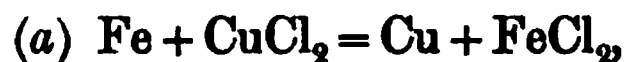
Two and a half litres of air were passed in eight minutes through the combustion furnace and a caustic potash bulb with a prolong holding only 2 inches of calcium chloride. The loss from imperfect dehydration was .0017 grams. A carbon residue from five grams of steel burned at the same rate, the carbon dioxide being absorbed in the same bulb, yielded 1.17 per cent. of carbon: numerous previous determinations had fixed the percentage at 1.18.

### 2. Imperfectly-filtered Carbon Residues.

Tungsten steels in particular which have been much worked may give a turbid filtrate when free acid and alkaline salts are nearly washed from the carbon residue. The turbidity is yellow, grey, or black, and may or may not contain carbon. Washing with alcohol or very dilute ammonium nitrate has been suggested to obviate this, but as the misfortune cannot be predicted it is as well when it does occur to complete the washing regardless of the turbidity, and then to pass the turbid liquid through a fine-grained and compact filter made from asbestos fibres which have been ground with a little water in a mortar. The small residue thus collected is burnt with the main carbonaceous mass, unless curiosity demands a separate combustion. The turbidity is frequently due to oxides of tungsten only.

### 3. Continued Use of the Solution of the Double Copper Salt.

Iron dissolves in copper solutions according to the following equations:



The ammonium, sodium, or potassium chloride is present chiefly for the purpose of retaining the cuprous chloride in solution.

The green copper solution begins to darken almost immediately it is brought into contact with the iron. This shows that the second reaction follows close on the heels of the first, because it is to the action between the copper and the copper ammonium chloride that the blackening is due, or, more strictly speaking, to the formation of cuprous in the presence of cupric chloride.

On dissolving metallic copper in an acid solution of cuprammonium chloride the colour changes are: Bright green, olive green, light brown (black in the mass), dark brown, and then, if the copper be in excess, reddish brown to a practically colourless solution of cuprous chloride. Both cuprous chloride and ferrous chloride oxidize readily in the air, so that when the dissolving steel is pneumatically agitated the reduced metallic salts get partially re-oxidized. By continuing to pass air the oxidation becomes so far complete that the solution regains its original green colour. The solution is also re-oxidized by simple exposure to the air. (See Bibliography, No. 62.)

The same 300 c.c. of a saturated acid solution of cuprammonium chloride were used to dissolve six separate five-gram lots of the same steel; the results obtained were 1.21, 1.19, 1.18, 1.20, 1.20, and 1.19 per cent. carbon. After the operation has been repeated four or five times there is a decided decrease in the rate at which the solution can be filtered, and during the dissolving of the eighth five grams the operation came to an end on account of the separation of crystals of the copper salt.

If neutral solutions of the double copper salt are used the oxidized iron is thrown out and makes a mess on the flask and tubes; if, however, the sample is dissolved by shaking in a stoppered flask the solution may be filtered without any appreciable amount of iron being thrown out. The filtrate can then be oxidized by the air current, the iron oxide allowed to settle, and the clear green solution used again. The following results were obtained by re-using the same solution for separate lots of the same steel: 1.184, 1.184, 1.178, 1.184 per cent. carbon.

By a system of fractional crystallization the bulk of the iron can be concentrated in a volume of mother-liquor some five or six times less than the original volume of the filtrates. Crops of crystals of more or less pure cuprammonium chloride which may be used again for dissolving steels are thus obtained.

#### 4. Bottle Labels.

The ordinary unprotected adhesive label does not long resist the attack of damp acid fumes which are always in the air of an active

laboratory. Of the varnishes, balsams, etc., used to coat the surface, paraffin wax is about the most handy and serviceable. This may be brushed over the label after melting, or the label itself after it has dried on the bottle may be heated in the bunsen flame and rubbed over with a piece of wax. Faraday recommended a mixture of Brunswick black with half its bulk of oil of turpentine ; the mixture to be kept in a bottle whose stopper was perforated with a thick-nibbed pen.

A most elegant label may be made by grinding sealing wax first dry and then mixed with a little alcohol and ether in such proportions as make a thick liquid. The lettering is done by means of a piece of glass tube drawn out at one end, the other end being attached to the mouth by a piece of rubber tubing, so that the wax can be gently forced out as needed. As the wax is not brittle when dry, it may be used for lettering note-books, etc. ; it may also be used for waxing such joints of glass apparatus as might be fractured by heating.

5. Reducing Action of Filter Papers.

The action of paper on permanganate solutions cannot be overlooked, but the reducing action of paper on hot dilute chromate solutions not only often passes unnoticed, but is occasionally said to be of no moment when pure papers are used. The following tests bearing on this point were made by Mr. Jervis.

25 c.c. potassium bichromate (1 c.c. = 0.01 gram of iron) were diluted to 200 c.c., heated in the water oven, a 12½ cm. paper added, and the digestion continued for half an hour. The acid series contains 50 c.c. normal sulphuric acid, the alkaline series 50 c.c. normal sodium hydrate. In a few cases the paper was added to the cold solution.

12½ Centimetre Paper.	Ash.	c.c. K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> after digesting.			
		Hot.		Cold.	
		Acid.	Alkaline.	Acid.	Alkaline.
English (Ford Mill, 428), . . .	0.0048	23.7	24.8	—	—
Schleicher & Schüll, No. 589, . . .	0.0002	23.8	24.2	25.0	25.0
Thin German (S. & S.), . . .	0.0028	24.2	24.6	—	—
Ordinary German, . . .	0.0028	23.6	24.6	25.0	25.0
Swedish (Munktell), . . .	0.0005	24.6	24.9	—	—
French white, . . .	0.0070	24.3	24.7	—	—
French grey, . . .	0.0139	22.5	24.1	24.4	24.7
White blotting paper (Ford Mill, 428),	0.0095	22.9	—	—	—



### 6. The Care of Platinum Apparatus.

Salts of easily reducible metals, such as tin, antimony, lead, etc., should never be heated in platinum vessels; nor should phosphates, as they tend to make the metal brittle. The element silicon, or rich ferro-silicon alloy, together with a flux, may also destroy platinum. Tungsten powders, too, or some constituent of them, will sometimes superficially attack or alloy with the platinum dish in which the roasting is made. Stains on crucibles and dishes are generally removed by digesting with hydrochloric acid alone, by digesting with hydrochloric acid after fusion with sodium carbonate, or by fusion with acid potassium sulphate.

The grey appearance of platinum which has been ignited for a long time has been shown by Erdmann to be really a superficial loosening of the texture of the platinum in consequence of the strong heat. This grey coating, which under the microscope appears rough and almost warty, disappears when the utensil is polished with fine sand, the weight lost in the operation being really insignificant. The regular cleaning of crucibles, therefore, not only retains a beautiful, smooth surface, pleasant to work with, but also preserves the metal.

Dishes and crucibles should never be needlessly bent out of shape. Small plugs or lasts for straightening them when crooked are cheap luxuries which the mental stimulus of working with trim and clean apparatus makes it worth while obtaining.

Small holes in the sides or other accessible places on dishes and crucibles can easily be patched with platinum foil as follows: Support the crucible over a clean iron rod of about its own curvature, clean with sand, lay on a piece of foil considerably larger than the hole, and direct a blow-pipe flame on the spot. By gently tapping with a hammer the weld becomes so perfect as to be scarcely distinguishable. In the same way scrap platinum can be made to serve many a useful end.

### 7. Filters and Filtering Operations.

**Pulp Filters.**—In some cases, mainly when large sticky precipitates are being dealt with, the cone filter, plain or ribbed, is very necessary, but for the majority of operations the pulp filter does the work more quickly and better. The pulp is made by tearing soft-textured ashless paper (we use Schleicher & Schüll's No. 589) into small pieces and soaking well with water in a stoppered flask; or to make large quantities the paper is kneaded in a jar with water and the small flask

filled up as required.<sup>1</sup> To make a filter, place a porcelain disc (a button is useful when discs are scarce) in the throat of the funnel, cover it with water and pour on the pulp; when the excess of water has run away press down the edges of the filter to prevent it rising during the filtration. If the filter is made at twice, it is easy when removing it from the funnel to split it, the upper part holding all the precipitate, and the lower being quite clean paper; it is sometimes convenient to do this.

The special advantages of pulp filters are:

1. A filtering medium of any desired texture can be made by applying more or less pressure.
2. The greater effect of a given amount of wash water, since every portion must pass through the precipitate.<sup>2</sup>
3. No fear that the precipitate may creep over the edges of the paper.

One drawback to the use of pulp is the impossibility of separating the precipitate from the paper. Happily the necessity of doing so is comparatively rare; much rarer in fact than is generally believed. Having regard to the ignition of a precipitate, pulp has this advantage: that by thorough aspiration the precipitate is sucked firmly on if not into the paper and is much less likely to spatter when dried hurriedly at the mouth of the muffle.

In transferring the filter to the crucible, which is done by turning up one edge of the filter with the leg of a pair of forceps, lifting it out, and cleaning with a piece of paper pressed against the revolving funnel, it is by no means easy to prevent the precipitate from touching the crucible at some point, and in this way the glaze is soon destroyed. To avoid this place a piece of ashless filter paper in the crucible and put the filter on it.

In handling an appreciably soluble precipitate, the beaker or flask should be cleaned with portions of the filtrate (which are already saturated solutions so far as the precipitate is concerned), and water or other wash liquid proper used to displace the mother liquor. It is better to wash many times with small quantities of liquid rather than a few times with large quantities.

**Accelerated Filtration.**—Pulp can be used under pressure with less than the usual danger of pulling the precipitate through or breaking

<sup>1</sup> Filter paper clippings are obtainable from S. & S. at less than one-tenth the price of the ordinary circles, and of course serve this purpose equally well.

<sup>2</sup> See theory of the washing of precipitates in Ostwald's *Scientific Foundations of Analytical Chemistry*.

the filter. An extempore suction can be provided by arranging a flask as usual for pressure filtering and sucking with the mouth through a piece of rubber tubing which is attached to the bent glass tube in the rubber stopper. In this way with a flask of several hundred c.c. capacity it is possible to obtain a vacuum equal to 12 inches of mercury, and as the vacuum is destroyed only by the wash water passing through the precipitate, one rarefaction can be made to serve for one complete washing. Ordinary rubber tubing closes up under a pressure of 9 to 12 inches of mercury.

There is a most excellent paper by Fairley (*Journal Soc. Chem. Ind.* 1887, page 64), "On the Various Forms of Filter Pumps or Water Jet Aspirators."

**A Syphon Filter.**—For the filtration of large volumes of reagents a syphon filter (see Fig. 83) is very useful. A perforated plate in the neck of the filter tube supports either paper or asbestos pulp. The syphon, on one leg of which is a rubber stopper, is filled with water, immersed in the liquid to be filtered, and then, as soon as all the water has been driven out, joined by the stopper to the filter tube.

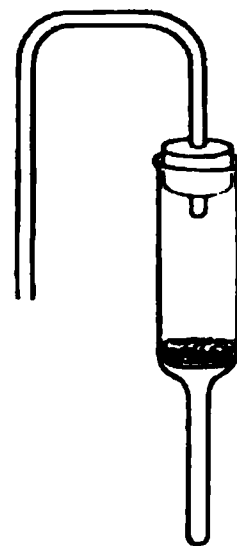


FIG. 83.

**The Gooch Crucible.**—An important form of filtration was suggested by Gooch, which involves the use of a platinum crucible having a perforated bottom on which is laid a coating of asbestos felt. Although for certain purposes it is invaluable, it is too expensive a piece of apparatus to be stocked for every-day use. A description of the crucible and the mode of using it, together with a few other of the numerous suggestions for filtering liquids, will be found in Crookes' *Select Methods in Chemical Analysis*.

**Adsorption of Salts by Filters.**—The adsorption of a salt from a solution during filtration can only very rarely occur to a noticeable extent. During fractional filtrations, however, it is well to bear the possibility of it in mind. Paper, for instance, adsorbs (*i.e.* takes up proportionally more of the salt than of the solution it is dissolved in) nickel and lead acetate; and sand filters adsorb the acetates of chromium, iron, and copper. It sometimes happens that a salt adsorbed in this way cannot be removed by washing, and almost invariably it happens that when a precipitate has been washed with water whose volume is  $(m-1)$  times the mother liquor held by the precipitate and filter the impurity still remaining has not been reduced to the  $m$ th part. The reason for this is that in contact surfaces between solids and liquids the concentration of the dissolved

substance is different from and always greater than in the rest of the solution. This consideration, by the way, explains why the fine powder of a crystalline precipitate gradually becomes coarser by digestion in the liquid. (See Ostwald's *Scientific Foundations of Analytical Chemistry*.)

**Preparing Asbestos for Filters.**—Cut the asbestos fibre into pieces half an inch long, cover with concentrated hydrochloric acid and keep in a warm place for several hours. Then transfer the asbestos to a funnel which contains a large filter plate and drain off and squeeze out the excess of acid. Transfer the asbestos to a sieve of about twenty meshes to the inch and vigorously agitate with a strong current of water until all free acid is washed out. Now squeeze as dry as possible, break into small pieces and ignite very strongly in the muffle. The ignited material may be used at once after shaking up with water; or if a more open filter is desired it is again washed into the sieve to get rid of the powdered portion. A filter made up with hot water acts more rapidly than if made with cold.

#### 8. Perforating Glass: A Gas Generator: Breaking Tubes.

Knowing how to make a hole through a glass plate or bottle enables one to build up neat arrangements of apparatus from common materials never intended for the purpose. To put a hole through a cover glass constitutes the simplest case and one often required where electrolytic analysis is practised; this is done as follows: Make a few scratches in the form of an asterisk with the point of a broken triangular file dipped in turpentine. Rest the cover on a wooden block or piece of cork, and turn the sharp point of the file backwards and forwards: a hole will be obtained in a minute or two. With sheet glass it is usually better to do the boring from each side. To pierce the side of a bottle make the asterisk and start the hole with the point of a triangular file. Then break the point off and work with the new and larger point until the indent is  $\frac{3}{8}$  or  $\frac{1}{2}$  inch in diameter. A smart tap will break the file as required, and the new edges are very able cutters. When the indentation is thus enlarged one of the sharp corners of a broken file can be used to groove it towards the centre with almost as much facility as a bradawl could be used on hard wood. A few turns of the file clears off the ridges and leaves the indent much deeper. When the hole is much cupped and nearly through strike it in the centre with the file tang; there must be no hesitation in giving the tap, and no blundering brute force. The hole is then widened by

working with a tapering file ; preferably a flat one, as it does not jam so readily. Porcelain can be similarly perforated.

Throughout the operations the tool should be moistened with turpentine or turpentine and camphor. Such articles as bottles are conveniently fixed in position, resting on a partly-opened heavy drawer. As an alternative the boring may be done under water in a wash basin or deep sink. In this way it is possible to shape sheet glass with a pair of scissors, but one must make haste carefully.

The gas generator (Fig. 84) is made in the above fashion from old reagent bottles, and it is as efficient as a Kipp.

Thick glass combustion tubing may be broken by heating a nicked portion between coils of wetted filter paper, by soaking twine with alcohol, wrapping it on the tube and lighting it, and in other ways. None, however, give such good results as the following :

Make a decided nick, and then complete the circle in a fainter line. Lay on the deeply-notched point a red hot quarter-inch iron rod, and keep it there until it blackens ; if the fracture has not already occurred touch the glass with the tip of a wetted finger. The fracture is in most cases as even as possible, but occasional irregularities are levelled up with the pliers ; the effect is greater and the danger of fracture less if the pliers are used from the outer diameter of the tube.

When working thinner tubing before the blow-pipe it may be broken by drawing the sharp *wetted* edge of the file lightly over the still hot glass.

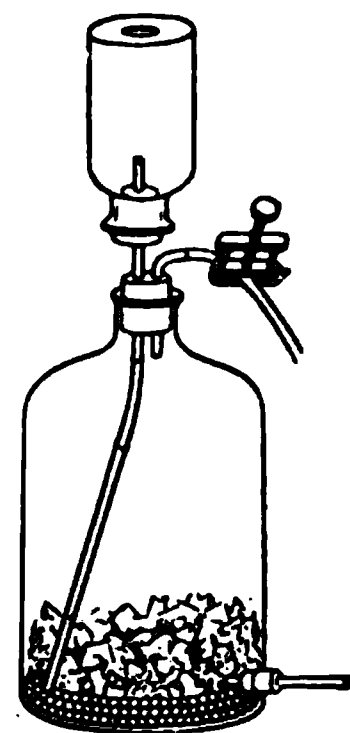


FIG. 84.

### 9. Hastening Evaporations.

Evaporations in either crucibles, dishes, or beakers may be hastened by blowing a stream of air—better if heated—over the surface of the boiling liquid ; in this way the operation may be safely conducted, when otherwise a great deal of spattering would occur. When a solution is being evaporated with a view to ignition of the residue, the evaporated surface may be increased by placing a piece of crumpled ashless paper so that it shall be almost wholly above the surface of the liquid.

### 10. Mixing Dry Powders.

Dry powders are more easily and thoroughly mixed by shaking in a stoppered bottle than by turning over and over again with a spatula.

The tall forms of weighing bottle are very convenient for use, and we find it well to retain a small one solely for shaking up powdered alloys which need combusting with some oxidizing reagent; and a larger one for mixing powdered materials with sodium carbonate, the tribasic reagent, etc.

### 11. Powdering Samples.

For crushing metallic alloys a steel mortar is indispensable. One of a convenient shape is shown in Fig. 85. It wears well if made from the best procurable chisel steel containing about 1.10 per cent. carbon. The separate parts are made to fit easily, and the faces of the mortar and pestle are hardened.

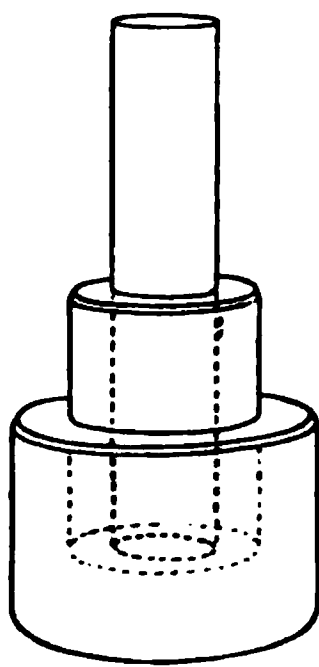


FIG. 85.

The pestle of an agate mortar can be used more effectively and with less labour if it is fitted into a file handle and fastened with shellac. The grinding of some powders in the 'agate' is much facilitated by moistening with water.

Earthenware mortars are generally too soft to be safely used for grinding samples; but it must not be forgotten that in this respect even they should sometimes be used in preference to the common bowl-shaped iron mortar. Both kinds are apt to be considerably abraded by the samples ground in them, and the nature of the impurity thus introduced is sometimes of great moment. For instance, magnesia or silica bricks crushed—as is by no means uncommon—in an iron mortar would pick up a considerable amount of metallic iron: the harder portion of the magnesia might be quite grey even through admixed iron before it was fine enough to pass a sixty-mesh sieve. In the subsequent analysis the ferric oxide would be considerably increased by this means, and a determination of the ferrous oxide would be hopelessly wrong. To minimize this error one may

1. Use a mortar made of hardened steel.
2. Powder as much as possible by stamping rather than grinding.
3. Go through the powdered sample with a magnet if it contains no other magnetic constituents.

By grinding ten grams of glass to a uniform size in mortars made of agate, bottle glass, hardened steel, and cast iron, Hempel found hardened steel to be undoubtedly the best material. The agate mortar lost eight times as much in weight as the steel mortar.

## 12. Repairing Furnace Casings (Fletcher's Instructions).

All internally fired refractory casings crack in use, generally at the first heating. The cracks are usually of no importance, and do not affect the working or permanence of the casing. Any repairs necessary can be made, or broken parts joined together by a freshly mixed paste of fluid silicate of soda with ordinary fire clay, the surfaces of the fracture being first moistened with the silicate solution to ensure adhesion. For furnaces working at very high temperatures no more of the solution should be used than is absolutely necessary. The furnace can be used at once without drying.

## 13. Sash Cords.

Even if no account be taken of the inconvenience of having repairs done, it is more economical to replace the ordinary sash cord by catgut of about the same thickness. The pulley over which the cord runs should be made entirely of brass. Friction may be minimized by coating the parts with black-lead.

## 14. The Constitution of Iron and Steel.

During recent years the researches of Carnot and Goutal have elucidated many points in the constitution of iron and steel materials. Their chief conclusions have been summarized as follows:<sup>1</sup>

*Sulphur* is usually combined nearly entirely with manganese as  $\text{MnS}$ , the excess, if any, being present as  $\text{FeS}$ .

*Phosphorus* is combined directly with iron as  $\text{Fe}_3\text{P}$ .

*Arsenic* is nearly always free, or exists as a solid solution, but after hardening it is partially combined with iron as  $\text{Fe}_2\text{As}$ .

*Silicon* is usually in the free state in cast irons. It can also unite with iron and manganese to form  $\text{MnSi}$  and  $\text{FeSi}$ , but the latter is dissociated on slow cooling or at least cannot then be isolated. The silicide  $\text{MnSi}$  is not dissociated by cooling. Ferro-silicons contain both  $\text{FeSi}$  and  $\text{Fe}_3\text{Si}$ .

*Carbon* is combined with both iron and manganese. In ferro-manganese it forms double carbides four of which the authors (C. & G.) have isolated:  $\text{Fe}_3\text{C} \cdot 4\text{Mn}_3\text{C}$ ;  $\text{Fe}_3\text{C} \cdot 2\text{Mn}_3\text{C}$ ;  $2\text{Fe}_3\text{C} \cdot \text{Mn}_3\text{C}$ ; and  $4\text{Fe}_3\text{C} \cdot \text{Mn}_3\text{C}$ . The latter appears to exist in pig irons and speigels; the excess of carbon exists in combination with iron as  $\text{Fe}_3\text{C}$ .

<sup>1</sup> *Journal Iron and Steel Institute*, 1901, i. 509.



The result is very striking if the ordinary analysis of a pig iron is arranged in accord with the above statements, thus :

	Per cent.
Combined Carbon, - - - - -	2·45
Graphite, - - - - -	0·60
Silicon, - - - - -	0·63
Manganese, - - - - -	2·00
Sulphur, - - - - -	0·12
Phosphorus, - - - - -	0·15
Arsenic, - - - - -	0·05
Iron, - - - - -	94·00
	<hr/>
	100·00

becomes

	Per cent.
Manganese Sulphide (MnS) - - - - -	0·33
Iron Phosphide (Fe <sub>3</sub> P), - - - - -	0·96
Manganese Silicide (MnSi), - - - - -	0·62
Carbide of Iron and Manganese (4Fe <sub>3</sub> C . Mn <sub>3</sub> C), - - - - -	7·48
Carbide of Iron, - - - - -	24·70
Carbon as an indefinite Sub-Carbide, - - - - -	0·32
„ as Graphite, - - - - -	0·60
Silicon, non-combined, - - - - -	0·42
Arsenic, free, - - - - -	0·05
Iron, free or as indefinite Hydride or Carbide, - - - - -	64·52
	<hr/>
	100·00

15. **Abstract of Franz Hundeshagen’s paper:** “Analytical Studies on Phospho-dodecamolybdic Acid, the Conditions of its Formation, and its separation as an Ammonium Salt.” (*Zeit. für Anal. Chemie*, xxviii. 141, and *Chemical News*, lx. 169, 177, 188, 201, and 215.)

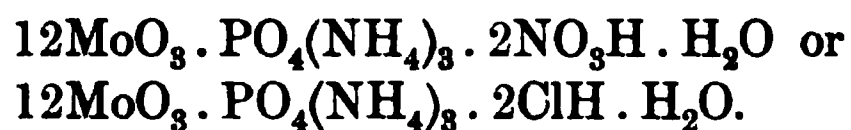
1. *Influence of the Nature of the Solution upon the Composition of the Precipitate.*

The composition of the precipitate obtained under the most varying conditions, if only free from molybdic acid and other impurities, after washing with cold dilute nitric acid and drying at 130°-150°, is in all cases (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub> . 12MoO<sub>3</sub>, whether the precipitation has been effected in strongly or slightly acid nitric, hydrochloric, or sulphuric solutions, containing more or less ammoniacal salt, dilute or concentrated, hot or cold solutions; and whether the phosphoric or molybdic acid was present in excess or not, or the solution contained a foreign salt (*e.g.* potassium) or not.

The precipitate obtained with excess of acid, washed with cold dilute



acid, and dried in the desiccator over calcium chloride or caustic potash to constant weight, contained two molecules of the acid, in the presence of which the precipitation ensued and which served for washing, and also one molecule of water; thus



Both acid and water are expelled quickly and completely at temperatures exceeding  $130^\circ\text{C}$ .

The methods of analyzing the phospho-molybdate are given here.

## 2. *Influence of the Proportion of Ammonium Nitrate in the Solution upon the Separation of the Precipitate.*

Phosphoric acid (sodium hydrophosphate) and molybdic acid (sodium molybdate) were present in some experiments in the proportion of 1 : 24, and in some cases in different proportions. The solutions were variously diluted, a measured amount of nitric acid added, the yellow liquid heated nearly to boiling, and a solution of ammonium nitrate gradually run in until the precipitate of phospho-molybdate no longer increased. The following phenomena were observed:—At first the precipitate disappeared again regularly a short time after the addition of every drop of the ammonium nitrate. It did not become permanent until a considerable part of the solution had been added, though it still increased visibly with every drop, and soon gave the solution a pale yellow milky appearance. In this state the liquid did not clear in the slightest even after prolonged heating, and on attempting to filter it ran through very turbid. A few more drops of ammonium nitrate condensed the precipitate and caused it to deposit, so that when viewed against a blue glass it appeared clear, and further addition of ammonium nitrate caused no precipitate: the phospho-molybdic acid was completely precipitated.

From these experiments it appears that, independent of the proportion of phosphoric, molybdic, and nitric acids, the amount of ammonium nitrate required was essentially the same, *i.e.* about 0.4 to 0.5 gram per 100 c.c. Below 0.4 gram the solution was milky; with more than 0.5 gram, the separation of the precipitate (except when less than 0.01 gram of phosphoric acid per 100 c.c. was present) was the more rapid the more phospho-molybdic acid was present.

In order to effect the most rapid separation of the phospho-molybdate, it seemed most convenient to have from 5 to 10 per cent. of ammonium nitrate. About three times as many molecules of potassium nitrate as

ammonium nitrate are needed to completely precipitate the phosphomolybdate.

### *3. Conditions of Temperature and Concentration.*

Under otherwise favourable conditions the temperature has no influence upon the completeness of the separation of the phosphomolybdate. The precipitation was the more rapid the more of the elements of phosphomolybdic acid were present, and the more strongly it was heated; 0.010 gram phosphoric acid ( $P_2O_5$ ) in 100 c.c. of liquid, which were completely precipitated from a hot solution in a few minutes, formed at common temperatures the first traces of a precipitate in the shape of delicate stripes and veils on the side of the glass after ten minutes with frequent stirring. (These cloudings appear most plainly on those parts of the vessel most heated by the proximity of the body.) The separation then became more copious and was almost complete in  $2\frac{1}{2}$  hours. Under certain circumstances a mechanical impulse is necessary to set the reaction going.

As to the physical properties of the precipitates obtained at different temperatures and under varying conditions, those thrown down from very hot and not too acid solutions by an excess of molybdic acid seemed on microscopic examination to be the most perfectly crystalline. The presence of a sulphate seems to favour the crystalline development of the precipitate, but delays its separation. The precipitate from a cold solution is composed of spheroidal granules of very different sizes: that from hot solutions is very uniform in its grain and consists of distinctly formed octahedra. This is the reason why the precipitate from a hot solution settles more quickly and completely, and can be more easily filtered and washed.

### *4. Influence of the Acidity of the Solution on the Formation of the Phospho-dodecamolybdate.*

If nitric acid is added to a hot neutral solution containing the elements of phospho-dodecamolybdic acid along with a suitable quantity of ammonium nitrate we observe:

At the first the liquid remains clear and colourless, but on further addition of acid there appear yellow colourations and turbidities, which disappear on stirring. Then follows a yellowing colour, growing more intense with incipient precipitation, then copious yellow deposits, which subside more and more perfectly as the acid is added. Finally, a visible precipitate is no longer produced; the separation is complete. A

further slight addition of the nitric acid has no influence on the precipitate, but a considerable excess produces a decomposition. This decomposing action is more manifest if the nitric acid is added to the phosphoric or molybdic acid before they are mixed.

The formation of the phospho-molybdate by adding nitric acid to a neutral mixture of phosphate and molybdate in molecular proportions is shown to take place in three phases corresponding to the addition of 15, 23, and 26 molecules respectively of nitric acid. Twenty-four molecules only should be required to form  $(\text{NH}_4)_3 \cdot \text{PO}_4 \cdot 12\text{MoO}_3$ ; the additional two are combined in an unstable form, as is represented at the beginning of this abstract. An excess of either component of phospho-dodecamolybdic acid in the original neutral solution involves an increased consumption of nitric acid; so that for every six molecules of ammonium molybdate there are required eleven molecules of nitric acid, and for each molecule of ammonium hydrophosphate about two molecules of nitric acid for the separation more than if the substances had been mixed in the exact proportion of  $\text{P}_2\text{O}_5 : 24\text{MoO}_3$ . This additional amount of nitric acid forms with the ammonium molybdate an acid ammonium molybdate containing only one molecule of the base to six of the molybdic acid, and with the hydrophosphate a dihydrophosphate. From these data the author concludes that the yellow precipitate should be a phospho-diexamolybdate.

In examining the dissociation of the phospho-molybdic acid under the influence of an excess of nitric acid by adding the required quantity of nitric acid to the mixture of ammonium molybdate and nitrate, running in the measured amount of phosphate solution and heating, it was found that the proportion  $\text{P}_2\text{O}_5 : 24\text{MoO}_3$  was maintained as before. When no further precipitate was deposited the filtrate was neutralized to the most desirable point of acidity, and any further precipitate determined. When from 26 up to 80 molecules of nitric acid were added no dissociation could be observed. With 100 molecules the dissociation was perceptible, and from this point it increased continuously and rapidly; in the presence of 1900 molecules no precipitate was formed, the dissociation being complete.

In parallel experiments made to determine how much molybdic acid was needed, at different degrees of acidity, to complete the precipitation, it was found that an excess (beyond the normal  $24\text{MoO}_3$  to  $1\text{P}_2\text{O}_5$ ) almost exactly equal to the molybdic acid which remained in solution through dissociation, was sufficient. In a solution of phosphate therefore which contains an excess of nitric acid there must exist, besides the quantity of  $\text{MoO}_3$  required to form the phospho-dodecamolybdate,

one molecule of  $\text{MoO}_3$  to every  $\frac{1900 - 26}{12} = 156$  molecules of free nitric acid in excess in order that the separation of the phosphorus may be complete.

*5. Influence of Foreign Salts upon the Formation and Separation of the Phospho-molybdate.*

As an excess of phosphate or molybdate in a neutral saline mixture involves an increased consumption of acid in the precipitation of the phospho-molybdate, so other salts of polybasic acids have a similar action. Indifferent salts of monobasic acids, *e.g.* chlorides and bromides, have no influence on the course of the reaction.

Of the former salts the author has studied ammonium sulphate and borax. He finds that sulphuric acid, added to a neutral solution containing the elements of phospho-dodecamolybic acid completes the formation when as many molecules were present as were required of nitric acid in previous experiments, but the conclusion of the reaction was not so distinct. Any excess of ammonium sulphate present necessitated the conversion of one-tenth part of it into ammonium hydrosulphate by the addition of extra acid before the precipitation could be completed. In the other case with borax, the additional acid required must be enough to convert the borax to boric acid.

*6. Action of Salts, Water, and Acids upon the pre-formed Phospho-molybdate.*

Perfectly neutral and cold solutions of ammonium nitrate and ammonium chloride do not dissolve any appreciable quantities of ammonium phospho-molybdate, but they eliminate the two loosely combined equivalents of acid, so that the precipitate after washing with the neutral saline solution is saturated by 23 molecules of alkali like the phospho-molybdate dried at  $150^\circ$ . Very dilute solutions dissolve the phospho-molybdate without decomposition, but it is re-precipitated on adding ammonium nitrate.

Nitrates and chlorides of sodium and of (in lesser degree) potassium transform the precipitate to a soluble phospho-molybdate, re-precipitated by ammonium salts.

By heating with water considerable amounts of phospho-molybdate can be dissolved in a short time; ammonium nitrate and nitric acid effect re-precipitation. Salts of organic acids dissolve the phospho-molybdate; it is re-formed, however, when the organic acid is monobasic

if it be set free by a mineral acid in the presence of ammoniacal salts. Polybasic organic acids, *e.g.* tartaric and oxalic, entirely prevent the re-union of the elements of the phospho-molybdate.

The precipitate is attacked by nitric, hydrochloric, and sulphuric acids in the order named. The most suitable acid and neutral solutions for washing the phospho-molybdate are given.

The paper closes with particulars of the estimation of phosphoric acid by titrating the neutral or faintly acid solution with definitely acidified solutions of molybdic acid. In an appendix there are particulars of Finkener's method of direct weighing of the phospho-molybdate and two indirect means of estimating it depending on (1) saturation with an alkali; (2) precipitation of the neutral solution with standard nitric acid.

HARDNESS TABLE.

Parts of Calcium Carbonate per 100,000.

c.c. of Soap Solution.	Parts of CaCO <sub>3</sub> .	c.c. of Soap Solution.	Parts of CaCO <sub>3</sub> .	c.c. of Soap Solution.	Parts of CaCO <sub>3</sub> .	c.c. of Soap Solution.	Parts of CaCO <sub>3</sub> .	c.c. of Soap Solution.	Parts of CaCO <sub>3</sub> .	c.c. of Soap Solution.	Parts of CaCO <sub>3</sub> .
0·7	0·00	3·3	3·64	5·9	7·29	8·5	11·05	11·1	15·00	13·7	19·13
0·8	0·16	3·4	3·77	6·0	7·43	8·6	11·20	11·2	15·16	13·8	19·29
0·9	0·32	3·5	3·90	6·1	7·57	8·7	11·35	11·3	15·32	13·9	19·44
1·0	0·48	3·6	4·03	6·2	7·71	8·8	11·50	11·4	15·48	14·0	19·60
1·1	0·63	3·7	4·16	6·3	7·86	8·9	11·65	11·5	15·63	14·1	19·76
1·2	0·79	3·8	4·29	6·4	8·00	9·0	11·80	11·6	15·79	14·2	19·92
1·3	0·95	3·9	4·43	6·5	8·14	9·1	11·95	11·7	15·95	14·3	20·08
1·4	1·11	4·0	4·57	6·6	8·29	9·2	12·11	11·8	16·11	14·4	20·24
1·5	1·27	4·1	4·71	6·7	8·43	9·3	12·26	11·9	16·27	14·5	20·40
1·6	1·43	4·2	4·86	6·8	8·57	9·4	12·41	12·0	16·43	14·6	20·56
1·7	1·56	4·3	5·00	6·9	8·71	9·5	12·56	12·1	16·59	14·7	20·71
1·8	1·69	4·4	5·14	7·0	8·86	9·6	12·71	12·2	16·75	14·8	20·87
1·9	1·82	4·5	5·29	7·1	9·00	9·7	12·86	12·3	16·90	14·9	21·03
2·0	1·95	4·6	5·43	7·2	9·14	9·8	13·01	12·4	17·06	15·0	21·19
2·1	2·08	4·7	5·57	7·3	9·29	9·9	13·16	12·5	17·22	15·1	21·35
2·2	2·21	4·8	5·71	7·4	9·43	10·0	13·31	12·6	17·38	15·2	21·51
2·3	2·34	4·9	5·86	7·5	9·57	10·1	13·46	12·7	17·54	15·3	21·68
2·4	2·47	5·0	6·00	7·6	9·71	10·2	13·61	12·8	17·70	15·4	21·85
2·5	2·60	5·1	6·14	7·7	9·86	10·3	13·76	12·9	17·86	15·5	22·02
2·6	2·73	5·2	6·29	7·8	10·00	10·4	13·91	13·0	18·02	15·6	22·18
2·7	2·86	5·3	6·43	7·9	10·15	10·5	14·06	13·1	18·17	15·7	22·35
2·8	2·99	5·4	6·57	8·0	10·30	10·6	14·21	13·2	18·33	15·8	22·52
2·9	3·12	5·5	6·71	8·1	10·45	10·7	14·37	13·3	18·49	15·9	22·69
3·0	3·25	5·6	6·86	8·2	10·60	10·8	14·52	13·4	18·65	16·0	22·86
3·1	3·38	5·7	7·00	8·3	10·75	10·9	14·68	13·5	18·81		
3·2	3·51	5·8	7·14	8·4	10·90	11·0	14·84	13·6	18·97		

TABLE OF APPROXIMATE ATOMIC WEIGHTS.

Name.	Atomic Weight.	Melting Point.
Aluminium, - - -	27·0	625° C.
Antimony, - - -	120·0	450°
Arsenic, - - -	75·0	—
Barium, - - -	137·0	—
Bismuth, - - -	208·5	266°·5
Calcium, - - -	40·0	—
Carbon, - - -	12·0	—
Chlorine, - - -	35·4	-75°
Chromium, - - -	52·0	—
Copper, - - -	63·5	1054°
Hydrogen, - - -	1·0	—
Iodine, - - -	126·8	114°
Iron, - - -	56·0	1600°
Lead, - - -	207·0	326°
Magnesium, - - -	24·0	800°
Manganese, - - -	55·0	—
Mercury, - - -	200·0	-38°·8
Molybdenum, - - -	96·0	—
Nickel, - - -	59·0	1500°
Nitrogen, - - -	14·0	—
Oxygen, - - -	16·0	—
Phosphorus, - - -	31·0	44°
Platinum, - - -	195·0	1775°
Potassium, - - -	39·0	62°
Silicon, - - -	28·4	—
Silver, - - -	108·0	960°
Sodium, - - -	23·0	92°
Sulphur, - - -	32·0	114°·5
Tin, - - -	118·5	225°
Titanium, - - -	48·0	—
Tungsten, - - -	184·0	—
Vanadium, - - -	51·3	—
Zinc, - - -	65·4	412°

TABLE OF FACTORS.

Element.	Found.	Required.	Factor.	Logarithm of Factor.
Aluminium, - -	$\text{Al}_2\text{O}_3$	Al	0.5294	$\bar{1}.72379$
Aluminium, - -	$\text{AlPO}_4$	Al	0.2213	$\bar{1}.34500$
Aluminium, - -	$\text{AlPO}_4$	$\text{Al}_2\text{O}_3$	0.4180	$\bar{1}.62121$
Bismuth, - - -	$\text{Bi}_2\text{O}_3$	Bi	0.8968	$\bar{1}.95269$
Calcium, - - -	CaO	Ca	0.7143	$\bar{1}.85387$
Calcium, - - -	$\text{CaSO}_4$	CaO	0.4118	$\bar{1}.61465$
Calcium, - - -	$\text{CaSO}_4$	Ca	0.2941	$\bar{1}.46852$
Carbon, - - -	$\text{CO}_2$	C	0.2727	$\bar{1}.43573$
Chromium, - - -	$\text{Cr}_2\text{O}_3$	Cr	0.6842	$\bar{1}.83519$
Chromium, - - -	Cr	$\text{Cr}_2\text{O}_3$	1.4615	0.16481
Copper, - - -	CuO	Cu	0.7987	$\bar{1}.90240$
Hydrogen, - - -	$\text{H}_2\text{O}$	H	0.1111	$\bar{1}.04576$
Iron, - - -	$\text{Fe}_2\text{O}_3$	Fe	0.7000	$\bar{1}.84510$
Iron, - - -	$\text{Fe}_2\text{O}_3$	FeO	0.9000	$\bar{1}.95424$
Lead, - - -	$\text{PbSO}_4$	Pb	0.6832	$\bar{1}.83453$
Lead, - - -	$\text{PbMoO}_4$	Pb	0.5640	$\bar{1}.75130$
Magnesium, - - -	$\text{Mg}_2\text{P}_2\text{O}_7$	MgO	0.3604	$\bar{1}.55674$
Manganese, - - -	$\text{Mn}_3\text{O}_4$	Mn	0.7205	$\bar{1}.85764$
Manganese, - - -	$\text{Mn}_3\text{O}_4$	MnO	0.9301	$\bar{1}.96854$
Manganese, - - -	Mn	MnO	1.2912	0.11090
Molybdenum, - - -	$\text{PbMoO}_4$	Mo	0.2616	$\bar{1}.41760$
Phosphorus, - - -	$\text{PbMoO}_4$	P	0.007	$\bar{3}.84751$
Phosphorus, - - -	$\text{PbMoO}_4$	$\text{P}_2\text{O}_5$	0.0161	$\bar{2}.20741$
Phosphorus, - - -	$\text{Pb}_3(\text{PO}_4)_2 \cdot 24\text{PbMoO}_4$	P	0.00644	$\bar{3}.80928$
Phosphorus, - - -	$\text{Pb}_3(\text{PO}_4)_2 \cdot 24\text{PbMoO}_4$	$\text{P}_2\text{O}_5$	0.0148	$\bar{2}.16916$
Phosphorus, - - -	$(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$	P	0.0165	$\bar{2}.21790$
Phosphorus, - - -	$(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$	$\text{P}_2\text{O}_5$	0.0378	$\bar{2}.57780$
Potassium, - - -	$\text{K}_2\text{PtCl}_6$	K	0.1607	$\bar{1}.20599$
Silicon, - - -	$\text{SiO}_2$	Si	0.4702	$\bar{1}.67228$
Sulphur, - - -	$\text{BaSO}_4$	S	0.1373	$\bar{1}.13779$
Sulphur, - - -	$\text{BaSO}_4$	$\text{SO}_3$	0.3433	$\bar{1}.53573$
Sulphur, - - -	$\text{PbMoO}_4$	S	0.0872	$\bar{2}.94048$
Titanium, - - -	$\text{TiO}_2$	Ti	0.6000	$\bar{1}.77815$
Titanium, - - -	$\text{TiO}_2$	$\text{TiO}_2 \cdot \text{P}_2\text{O}_5$	2.775	0.44326
Tungsten, - - -	$\text{WO}_3$	W	0.7931	$\bar{1}.89933$
Tungsten, - - -	$\text{WO}_3$	$\text{PbWO}_4$	1.961	0.29252
Tungsten, - - -	$\text{WO}_3$	$\text{Na}_2\text{WO}_4$	1.267	0.10286
Tungsten, - - -	$\text{PbWO}_4$	W	0.4044	$\bar{1}.60681$
Tungsten, - - -	$\text{PbWO}_4$	$\text{WO}_3$	0.5099	$\bar{1}.70748$
Vanadium, - - -	$2\text{Pb}_2\text{V}_2\text{O}_7 \cdot \text{PbO}$	V	0.1386	$\bar{1}.14186$
Vanadium, - - -	$2\text{Pb}_2\text{V}_2\text{O}_7 \cdot \text{PbO}$	$\text{V}_2\text{O}_5$	0.2467	$\bar{1}.39221$
Vanadium, - - -	$\text{V}_2\text{O}_5$	V	0.5619	$\bar{1}.74965$





**APPENDIX.**

**A BIBLIOGRAPHY OF STEEL-WORKS' ANALYSIS**

**BY**

**HARRY BREARLEY.**



## PREFACE.

THE following Bibliography was originated by an ambition to become personally acquainted with every known process for the estimation of manganese in minerals and metals, but particularly in steel-works' materials. Before the ambition could be realized it appeared that greater advantage was obtainable by taking in all the elements generally estimated in steel-works' materials and making only such experiments as were needed to assist the understanding.

In order to carry out the above idea, such sets of journals as were available were gone through and an orderly arrangement made of all relevant papers. Many irrelevant papers and series of lectures were also read, either because they were comprehensive demonstrations of every-day phenomena, or of physical and chemical laws, or because they were models of prolonged and delicate investigations.

Such a Bibliography is necessarily of most value to the compiler of it, but it may be of considerable value to others also, and therefore the various parts were published in the *Chemical News* at intervals between November, 1899, and March, 1902. They are collected here and brought up to the end of 1901 at the request of many—often personally unknown—friends who wished to have the complete Bibliography in a handy form.

The compilation is made from the following journals :

*Chemical News*, from vol. i. (1860).

*Journal of the Society of Chemical Industry*, from vol. i. (1882).

*Journal of the Iron and Steel Institute*, from 1880.

*Journal of the Chemical Society*, from vol. xlvii. (1885).

Owing to the numerous reprints and abstracts these journals contain the area covered is a very large one. The source of the reprint or abstract is not given ; this is a serious bibliographical error, but the aim of making the work of practical value is probably more nearly reached than it would be by numerous references to foreign journals,

which even if they were accessible—as is rarely the case in the neighbourhood of steel works—would be unintelligible to many analysts. It will of course often be found necessary to refer through the abstract to the original paper.

If a reprint is available it is referred to. Where there are only abstracts reference is made to one journal only, but in many cases a similar abstract may be found in the corresponding volume of the other journals.

H. B.

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## **CARBON.**

PAPERS on the relation of carbon to iron, its mode of existence after various kinds of physical treatment, etc., have been almost entirely neglected.

The processes for estimating  $\text{CO}_2$  in various solid, liquid, and gaseous compounds and mixtures have also been neglected, either because they are more properly treated in another section, or are only of second-rate interest in the steel works' laboratory. For a like reason, a large number of papers on organic analysis—of which the estimation of carbon after its separation from iron is but a particular case—are not referred to. These omissions are not intended to suggest what may and what may not be neglected in an analyst's equipment. Some such omissions were, however, necessary in a compilation which aims at making each reference bear directly on the practice of steel works' laboratories.

The following is the classification adopted :

### **I. DIRECT COMBUSTIONS.**

- a.* Dry Way.
- b.* Wet Way.

### **II. MODES OF RELEASING THE CARBON.**

### **III. ESTIMATING THE LIBERATED CARBON.**

- a.* By Weighing the Dried Residue.
- b.* Dry Combustion of the Residue.
- c.* Wet Combustion of the Residue.
- d.* Volumetric Estimation of the Residue.

### **IV. COLORIMETRIC ESTIMATION.**

- a.* Eggertz Process and Modifications.
- b.* Tintometers and other Apparatus.

### **V. OTHER PROCESSES FOR ESTIMATING CARBON.**

### **VI. ESTIMATION OF GRAPHITE.**

### **VII. MISCELLANEOUS NOTES.**

### I. Direct Combustion of the Sample.

#### a. In the Dry Way (see also 58, 84, 126, 184):

1. MULDER (*C. N.*, v., 5 and 210).—Cast-iron mixed with pumice stone is burned in oxygen. Regnault's mixture of  $\text{KClO}_3$  and  $\text{PbCrO}_4$  does not liberate chlorine.
2. HERMANN (*C. N.*, xl., 263).—Direct combustion in O in a short platinum tube. The  $\text{Fe}_2\text{O}_3$  formed verifies completeness of the combustion.
3. FÖRSTER (*J. I. S. I.*, 1895, ii., 588).—Ignite with  $\text{PbCrO}_4$  in small porcelain retort. Large pieces of iron are oxidized more readily than very fine powder.
4. LORENZ (*J. C. S.*, lxiv., ii., 291 ; and lxvi., ii., 119).—Mixture of steel and  $\text{PbCrO}_4$  ignited to white heat in oxygen.
5. LJUBAVIN (*C. N.*, lvii., 221).— $\text{PbCrO}_4$  may evolve  $\text{CO}_2$  on ignition ; it should be fused in a Cu crucible. Or KHO (Phipson, *C. N.*, xxi., 253), which causes low results.
6. PETTERSSON (*J. I. S. I.*, 1890, ii., 852).—Steel decomposed with  $\text{KHSO}_4$  ;  $\text{CO}_2$  and  $\text{SO}_2$  absorbed in  $\text{NaHO}$  and  $\text{Ba}(\text{HO})_2$  ;  $\text{SO}_2$  oxidized to  $\text{SO}_3$  and  $\text{CO}_2$  liberated with acid. Graphite is collected in a Pt funnel and burned in air and nitrous fumes. Later (*J. I. S. I.*, 1893, ii., 527),  $\text{SO}_2$  is retained by  $\text{CrO}_3$  and gases passed over  $\text{CuO}$  into  $\text{Ba}(\text{HO})_2$ .
7. BLAIR (*J. S. C. I.*, 1901, 70).—C in ferro-chromium estimated by fusing with  $\text{KHSO}_4$ .
8. SCHNEIDER (*J. I. S. I.*, 1894, ii., 488).—The filings are indirectly oxidized by igniting with metallic Pb or Cu. Carbide carbon is separated from iron with very dilute  $\text{H}_2\text{SO}_4$ . Later (*J. I. S. I.*, 1896, i., 531), purified phospho-copper is used instead of powdered Cu.
9. BREARLEY and LEFFLER (*C. N.*, lxxv., 241, 263, etc.).—Carbon in ferro-chromium can be estimated by igniting with  $\text{PbCrO}_4$ ,  $\text{CuO}$ , or  $\text{PbO}_2$ .  $\text{PbCrO}_4$  and  $\text{CuO}$  require high temperatures,  $\text{PbO}_2$  does not.
10. ROZYETI (*J. S. C. I.*, 1899, 865).—Direct ignition of fine steel borings or powdered ferro-chromium with pure  $\text{Al}_2\text{O}_3$  ; the process completed in thirty-five to ninety minutes.
11. SANITER (*C. N.*, lxxv., 287 and 311).—Ignites with a mixture of litharge and  $\text{CuO}$ .
12. BREARLEY (*C. N.*, lxxxi., 91).—Distinguishes between steel-making alloys where C is obtainable by direct ignition alone and those requiring a reagent.
13. BREARLEY (*C. N.*, lxxxiv., 23, 46, and 59).—Summarizes reagents proposed for direct combustion. Advantages of  $\text{Pb}_3\text{O}_4$  and  $\text{Bi}_2\text{O}_3$ .
14. BLOUNT (*J. I. S. I.*, 1900, ii., 573).—Steel filings are completely decarbonized at  $1100\text{--}1200^\circ\text{C}$ . Tubes are liable to fracture at such temperatures.
15. PARRY (*J. I. S. I.*, 1880, 442).—Has always been able to detect CO in steel. (Would this heighten the results obtained by direct combustion? —H.B.).



16. FUNK (*J. C. S.*, lxx., ii., 274).—The C in Zn is determined by direct combustion in oxygen.

*b. In the Wet Way:*

17. JUPTNER (*J. I. S. I.*, 1883, 779).—The sample is digested with  $\text{CrO}_3$  and a large amount of  $\text{H}_2\text{SO}_4$ . The evolved gases are dried and passed through KHO (see 184).
18. GMELIN (*J. I. S. I.*, 1885, 246).—Very much like Juptner's process.
19. HEMPEL (*J. I. S. I.*, 1895, i., 503).—Decompose sample with  $\text{CrO}_3$  and  $\text{H}_2\text{SO}_4$  in the presence of Hg; measure the  $\text{CO}_2$  evolved, after exploding in a pipette to destroy hydrocarbons. No hydrocarbons are evolved on treating grey pig-iron.
20. WIBORG (*J. S. C. I.*, 1887, 748; and 1890, 768).—Treat Fe with  $\text{CuSO}_4$ , and, without filtering, oxidize C with  $\text{CrO}_3 + \text{H}_2\text{SO}_4$ ; measure  $\text{CO}_2$  in tube. The deposited Cu protects Fe from acid until a high temperature is reached; at lower temperatures hydrocarbons are evolved.
21. VON REIS (*J. I. S. I.*, 1888, i., 376; and 1889, ii., 475).—Describes and commends Wiborg's process.
22. JUPTNER (*J. C. S.*, lvi., 186).—Describes Wiborg's process.
23. LUNGE and MARCHLEWSKI (*J. C. S.*, lxiv., ii., 45; lxxiv., ii., 188; and *J. I. S. I.*, 1894, ii., 484).—Modified Wiborg process.  $\text{H}_2\text{O}_2$  is used to generate O in the liquid, so as to expel  $\text{CO}_2$ . Separation of Fe with Cu solution and wet combustion of residue inaccurate (see also *J. C. S.*, lxii., 531).
24. DONATH and ERLLENHOFER (*J. I. S. I.*, 1897, ii., 496).—A modification of Wiborg's process.
25. REINHARDT (*J. I. S. I.*, 1892, ii., 511).—Gases burned to  $\text{CO}_2$  by passing over electrically heated Pd spiral, and measured over Hg. Later (*J. I. S. I.*, 1893, i., 403) uses heated platinized asbestos or prepared pumice.
26. BLAIR (*J. C. S.*, lxx., ii., 544).—A modified Wiborg process. Combustion made with  $\text{CrO}_3 + \text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4$ , and  $\text{CO}_2$  measured over Hg.
27. ROUFF (*J. S. C. I.*, 1899, 176).—Sample decomposed with  $\text{CuSO}_4$  and a mixture of sulphuric, chromic, and phosphoric acids. The evolved  $\text{CO}_2$  is measured. Not so good for ferro-alloys as for steels.
28. CAMPREDON (*J. S. C. I.*, 1898, ii., 84).—Uses Wiborg's process after separating the C or graphite.
29. KOCH (*J. S. C. I.*, 1894, 979).—Like Juptner, but passes gases over hot CuO. Special apparatus illustrated. See also WUST (*J. S. C.*, lxx., 449); GOCKEL (*J. S. C. I.*, 1900, 1041); and SCHMITZ (*J. S. C. I.*, 1901, 934).
30. VON REIS (*J. I. S. I.*, 1894, ii., 485).—Hydrocarbons are given off from direct combustion with  $\text{CrO}_3$  and  $\text{H}_2\text{SO}_4$ ;  $\text{H}_2\text{SO}_4$  absorbs them; therefore dries with phosphoric anhydride instead. Addition of  $\text{CuSO}_4$  lessens evolution of hydrocarbons. A constant error of 2 per cent. is allowed for. (See also *J. I. S. I.*, 1888, i., 374.) Pumice moistened with KHO a better  $\text{CO}_2$  absorbent than KHO bulb.

31. WOOD (*J. S. C. I.*, 1884, 652).—Decompose sample with acid, pass gases through  $\text{H}_2\text{SO}_4$ , alkaline Pb solution, and combustion tube into KHO. (See also 68, 70.)

## II. Modes of Releasing the Carbon.

32. WEYL (*C. N.*, v., 170).—The sample is made the + pole of a dilute HCl cell. C residue retains form of the sample. The process was previously suggested by Binks (*C. N.*, v., 252).
33. OSMOND and WERTH (*C. N.*, lvi., 35).—Re-heated steel attacked by Weyl's process leaves a C-Fe residue which is explosive or spontaneously combustible.
34. BLOUNT (*C. N.*, lvii., 28).—Place borings on Pt plate in Cu solution, and suspend Cu plate thereover. Pass current so that Cu is removed from borings nearly as quickly as it is deposited on the upper plate. Escape of hydrocarbons thus obviated.
35. JUTSUM (*C. N.*, xli., 17).—Solution in acid Cu solution leads to loss through evolution of hydrocarbons. Uses Weyl's process. Rubber to limit action to a portion of the rod. Filters through a straight tube plugged with muslin, sand, etc. KHO containing  $\text{KNO}_3$  absorbs O, and unduly increases the result.
36. HARTLEY (*C. N.*, xvi., 157).—The gas liberated in Weyl's process may be such as was occluded by the iron.
37. BOUSSINGAULT (*C. N.*, xvii., 267).—Powdered sample triturated with  $\text{HgCl}_2$ , the  $\text{HgCl}_2$  volatilized in a current of H, and dried residue weighed.
38. BOUSSINGAULT (*J. I. S. I.*, 1886, 822).—Above process fails if more than 2 per cent. Cr is present. Burns directly in O for thirty hours, or separation of Fe with Cl. FeW and FeMn are decomposed by the latter method.
39. FRESSENIUS (*C. N.*, xxi., 167).—Volatilize Fe with Cl. The chlorine must be thoroughly dry. See also NAUMANN and MUDFORD (*J. C. S.*, lxxii., ii., 209).
40. FRESSENIUS and HINTZ (*C. N.*, lxi., 67).—Release the C from FeCr in a current of Cl, and burn with  $\text{CrO}_3$  and  $\text{H}_2\text{SO}_4$ . Graphite is determined on 10 grms. of the sample after digesting for weeks in oft-renewed HCl.
41. WATTS (*C. N.*, xlv., 279).—Discusses various modes of releasing the C. Volatilize Fe with Cl in fifteen minutes; describes apparatus and precautions.
42. GINTL (*J. I. S. I.*, 1885, 589).—Chlorine should be passed over heated charcoal before being used to decompose the sample. When Fe is rich in manganese  $\text{MnCl}_2$  envelopes the C residue, and necessitates the subsequent use of a Cl absorbent.
43. SCHUTZENBERGER and BOURGEOIS (*C. N.*, xxxi., 207).—White cast-iron decomposed with  $\text{CuSO}_4$  and an acid solution of  $\text{Fe}_2\text{Cl}_6$ . The dried residue is a hydrate of carbon.

44. HOGG (*C. N.*, lviii., 199).— $\text{Fe}_2\text{Cl}_6$  may be used to decompose the precipitated Cu, or initially with the heated copper solution. If used alone it causes loss of C. Siliceous steels filter badly after standing.
45. ZABOUDSKY (*C. N.*, l., 57).—Triturates in a pasty mass of cuprasodium chloride. Cu dissolved with  $\text{Fe}_2\text{Cl}_6$ . Results of the colour process not comparable if metals are of different origin.
46. LANGLEY (*C. N.*, lxii., 227).—"International Standards" work. Values from 1.02 to 1.15 per cent. due to use of variously crystallized, acidified, etc., Cu solutions.
47. LANGLEY (*J. I. S. I.*, 1891, ii., 321).—Above results due to tarry matter (pyridine) in cuprammonium salts. Recommends cuprapotassium salts.
48. DROWN (*C. N.*, lxix., 5).—Acidified  $\text{CuCl}_2$  promptly dissolves the iron and gives good results.
49. ARNOLD (*Steel Works Analysis*, p. 29).—Has observed bubbles of gaseous hydrocarbons on using acid  $\text{CuCl}_2$  (see 337).
50. DUDLEY and PEASE (*J. I. S. I.*, 1894, i., 609).—Decompose Fe with cuprapotassium chloride. Duplicates agree to 0.005 per cent.
51. CARNOT and GOUTAL (*J. C. S.*, lxxii., ii., 520).—Dissolve in cuprapotassium chloride in an atmosphere of  $\text{CO}_2$  at  $90^\circ\text{C}$ . The *moist* residue is burned in oxygen.
52. CARNOT and GOUTAL (*J. S. C. I.*, 1899, 521).—Blair's recommendation—dissolving in an HCl solution of cuprapotassium chloride—leads to loss at temperatures of  $70^\circ$  and over. Dissolving in faintly acid solutions at  $95^\circ$  in atmosphere of  $\text{CO}_2$  rapid and reliable, except for Fe-Mn.
53. GALBRAITH (*C. N.*, xxxv., 151).—The iron of chromium steels refuses to replace copper in the solution. (This certainly is not the case with cuprammonium chloride.—H. B.).
54. FÖRSTER (*C. N.*, lxxii., 293).—Some kinds of wrought iron, and tungsten steels especially, evolve hydrocarbons on being dissolved in a quite neutral solution of cuprammonium chloride. Cuprammonium oxalate is suggested.
55. BRAND (*J. I. S. I.*, 1887, ii., 364).—On separating the C with neutral or basic cuprammonium chloride, hydrocarbons are evolved, and tungsten steels are hardly worse than other kinds. The loss is very serious in low-carbon steels.
56. BRAND (*J. C. S.*, lii., 866).—Decompose with HCl containing 24 per cent. Br; destroy Br with ammonium oxalate. Use Ag spiral in combustion-tube to retain traces of Br.
57. MOISSAN (*J. C. S.*, lxx., ii., 339).—Carbon is liberated from Al with  $\text{HgCl}_2$ , Hg volatilized in H, and residue burned in oxygen (see 37). GONTHIERE (*J. S. C. I.*, 1896, 830) uses cuprammonium chloride and wet combustion for Al and alloys.
58. BLAIR (*C. N.*, lxiv., 66).—The HCl solution gives higher results than the neutral solution of cuprammonium chloride. Determines C by direct combustion and volatilizing Fe in HCl. Cuprous chloride and

- anhydrous  $\text{CuSO}_4$ , the most efficient purifiers of  $\text{CO}_2$ . Repetition of Dudley's work (46).
59. GIRARD (*J. I. S. I.*, 1899, i., 464).—Uses the cuprammonium chloride process for estimating C in FeCr or FeSi, for which the chromo-sulphuric acid process is not satisfactory.
  60. BREARLEY (*C. N.*, lxxiv., 63). The dissolving sample is kept stirred by attaching the containing flasks, fitted with tubes, to the filter-pump. Vigorous shaking in a closed flask prepares a sample for wet combustion in fifteen minutes.
  61. J. T. (*C. N.*, lxxix., 169).—Accessory to above stirrer. Examination of the decomposition of steels with cuprammonium chloride and continued re-use of the same liquor.
  62. SARGENT (*J. S. C. I.*, 1900, 692).—Re-oxidizes cuprapotassic chloride for further use by passing  $\text{Cl}_2$ .
  63. BECKLINGHAUSEN (*J. C. S.*, lxxii., ii., 19).—A shaking apparatus, driven by a small motor.
  64. DUNSTAN and DYMOND (*C. N.*, lxx., 148).—A simple shaker, also driven by a motor.
  65. WIDOWISZEWSKI (*J. I. S. I.*, 1898, ii., 555).—Dissolves the sample of steel in cuprammonium chloride with a shaking apparatus in five to eight minutes.
  66. ZABOUDSKY (*J. I. S. I.*, 1882, 357).—After treating white pig-iron with  $\text{CuCl}_2$  the residue is  $\text{C}_{12}\text{H}_5\text{O}_3$ . It can be easily nitrated.
  67. ZABOUDSKY (*J. I. S. I.*, 1884, 297).—Liberated with  $\text{CuSO}_4$  and  $\text{NaCl}$ ; the dried residue contains varying percentages of C, according to the nature of the sample. Extremes, 65.5 to 71 per cent.
  68. DONATH (*J. I. S. I.*, 1898, i., 431).—Examination of the C residue. Nitro-derivative prepared therefrom identical with the substance giving Eggertz colour. All the combined carbon is not evolved on dissolving in dilute acid.
  69. JUFTNER (*J. I. S. I.*, 1896, ii., 422).—*Résumé* of the examinations made of the carbonaceous residue, gases liberated on dissolving steel and the state in which C exists in steel.
  70. BACKSTRÖM and PAJUKALL (*J. C. S.*, liv., 420).—Volume and character of gases evolved on decomposing steel with acids; liquid hydrocarbons formed.

### III. Estimating the Liberated Carbon.

#### a. Weighing the Dried Residue:

71. EGGERTZ (*C. N.*, vii., 254).—Iron separated with iodine and dried residue weighed, or Fe separated with  $\text{CuCl}_2$  and residue combusted. Graphite separated with  $\text{HCl}$ ; residue dried, weighed and ignited. Describes also the colour process and some of its limitations. Later (*C. N.*, xiv., 173) uses iodine dissolved in ferric iodide for separating the carbon.

72. WITTSTEIN (*C. N.*, xxii., 311).—Dissolve in  $\text{CuSO}_4 + \text{CuCl}_2$ , weigh dried residue. Loss on ignition = C (see 67).
73. BOUSSINGAULT (*C. N.*, xxii., 317).—Separates with  $\text{HgCl}_2$  (37); ignite residue at dull red; loss = carbon. Ignite in O current; loss = graphite.
74. HEID (*C. N.*, lxxvi., 183).—After treating with alcohol and ether, the residue, dried at  $120^\circ \text{C}$ ., is ignited; loss = C. Graphite estimated similarly. See also HERTING (*J. C. S.*, 78, 11, 245).
75. DOUGHERTY (*C. N.*, lxxx., 121, 146, 242, and 266).—Liberated carbon washed with hot dilute  $\text{HNO}_3$ , dried, and ignited; loss  $\times 0.675 = \text{C}$ . Graphite similarly. Not available for FeMn. See also AUCHY (*J. I. S. I.*, 1900, 574).

*b. Dry Combustion of the Residue:*

76. ABEL (*C. N.*, vi., 133).—Dissolve in acid  $\text{CuCl}_2$  (see 49), and burn residue with  $\text{CuO}$ . Liberate graphite with  $\text{HCl}$ , separate  $\text{SiO}_2$  with  $\text{KHO}$ , dry, and weigh.
77. TOSH (*C. N.*, xvi., 67).—Describes Regnault's (combustion with  $\text{PbCrO}_4$  and  $\text{KClO}_3$ ), Fresenius's (dissolve in  $\text{H}_2\text{SO}_4$ , pass gases over  $\text{CuO}$ , and estimate C in residue), Wohler's (separation of Fe with Cl, and combustion of the residue), and Weyl's (32). Critical remarks on each process.
78. FORBES (*C. N.*, xvi., 105).—Mainly like Abel (76). Dissolving for ten days.
79. PIESSE (*C. N.*, xxviii., 198).—Decompose with warm *acid* cuprasodium chloride (see 52). Burn residue with  $\text{CuO}$ .
80. TURNER (*C. N.*, lii., 15).—Decompose with cuprammonium chloride (see 184). The filter-tube is also the combustion-tube when resting on a small sheet-iron stand.
81. CLEMENCE (*C. N.*, xlviii., 206).—Also burns the C in the (platinum) filtering-tube.
82. DEVILLE and TROOST (*C. N.*, vii., 294), and RANDALL (*C. N.*, 76, 168).—Platinum tubes are porous to gases and vapours at high temperatures.
83. LANGLEY (*C. N.*, lxii., 218, and *J. I. S. I.*, 1890, ii., 583).—"International Standards" work. The  $\text{CO}_2$  is purified with  $\text{CuO}$ , Ag,  $\text{Ag}_2\text{SO}_4$  or  $\text{CuSO}_4$  pumice, and  $\text{CaCl}_2$  before being absorbed. An acid Cu solution gives higher results than a neutral one. Anhydrous  $\text{CuSO}_4$  pumice soon becomes inefficient.
84. SHIMER (*C. N.*, lxiv., 43).—Akin to Langley's paper. Direct combustion of the same samples. After liberal use of  $\text{HCl}$  all chlorides may be washed from the C residue.
85. DROWN (*C. N.*, lxix., 4).—Oxygen passed over hot  $\text{CuO}$  before using. Cl retained by Ag,  $\text{FeSO}_4$ , and anhydrous  $\text{CuSO}_4$ .  $\text{KHO}$  bulb absorbs all the  $\text{CO}_2$  (see 113), and  $\text{CaCl}_2$  prolong all the moisture.
86. SHIMER (*J. S. C. I.*, 1899, 863, and *J. C. S.*, lxxx., ii., 477).—The combustion is successfully made in an ordinary platinum crucible fitted with a water-cooled stopper. Apparatus serviceable for other operations generally requiring a tube.

87. DUPRÉ and HAKE (*C. V.*, xliii., 69).—Absorb  $\text{CO}_2$  in baryta water, convert  $\text{BaCO}_3$  to  $\text{BaSO}_4$ .  $\text{BaSO}_4$  weighs 19.4 times as much as the original carbon.
88. GOOCH and PHILPS (*C. V.*, lxxii., 194).—Estimation of  $\text{CO}_2$  as in 87. Special apparatus to collect  $\text{CO}_2$ .  $\text{BaCO}_3$  washed under a protecting layer of xylene.
89. PHILPS (*C. V.*, lxxiv., 65).—Estimates excess of  $\text{Ba}(\text{HO})_2$  with iodine and arsenious acid.
90. RICHARDSON (*J. C. S.*, lxx., 469).—Apparatus for absorbing  $\text{CO}_2$  in  $\text{Ba}(\text{HO})_2$ .
91. HANDY (*J. I. S. I.*, 1895, ii., 589).—Absorbs  $\text{CO}_2$  in  $\text{Ba}(\text{HO})_2$  and weighs  $\text{BaCO}_3$  or titrates excess with  $\text{H}_2\text{SO}_4$ .
92. MOISSAN (*C. V.*, lxxii., 2).—Carbon is separated from Mo with  $\text{Cl}_2$  and the residue combusted; or sample decomposed with acid in a stream of oxygen which passes over  $\text{CuO}$  into  $\text{KHO}$ . The graphite is determined in the residue.
93. BENNEVILLE (*J. I. S. I.*, 1895, i., 230).—C liberated with  $\text{Cl}_2$  mixed with  $\text{PbCrO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ , and burned.
94. BLOCHT (*C. V.*, lvii., 27).—Irregular results of Fresenius's process (77) due to formation of liquid hydrocarbons. (See 68 and 70.)
95. PHILLIPS (*J. I. S. I.*, 1887, ii., 372).—A solution of  $\text{KHO}$  in glycerin is used to absorb  $\text{CO}_2$ .
96. BAKER (*J. C. S.*, li., 253).—Carbon containing moisture gives rise to  $\text{CO}_2$  when heated at  $100^\circ \text{C}$ .
97. STOKES (*C. V.*, lvii., 150).—Uses asbestos instead of clay tiles, and an iron combustion tube closed with brass cap and leaden washer.
98. JERVIS (*C. V.*, lxxvii., 5).—Arched asbestos cover for combustion furnace.
99. WHITE (*C. V.*, xlii., 65).—An asbestos stopper made by pressing the moistened fibres into a mould.
100. DROWY (*C. V.*, lvii., 223).—Uses a funnel with so wide a stem that the dried asbestos and residue can be pushed down it into the combustion-tube.
101. BRENNEMAN (*C. V.*, xlviii., 168).—A platinum cylinder fitted with a perforated disc acts both as filter and boat.
102. CARUS (*C. V.*, iii., 66).—The  $\text{CO}_2$  is freed from  $\text{SO}_2$  by passing through heated  $\text{PbCrO}_4$ .
103. ETARD (*C. V.*, xlvii., 178).—Uses pumice soaked with  $\text{Cu}(\text{NO}_3)_2$  and ignited to provide the  $\text{CuO}$ .
104. KNOT (*C. V.*, iv., 13).—Collects rapidly evolved  $\text{CO}_2$  in a rubber bag, and subsequently passes it through  $\text{KHO}$  (see *C. V.*, lxxv., 241).
105. RUSSELL (*C. V.*, xvii., 260).—India-rubber absorbs notable amounts of  $\text{CO}_2$ .
106. WILLIAMS (*C. V.*, xliii., 69).—Black rubber is very pervious to  $\text{CO}_2$ . See also KOBBE (*J. S. C. I.*, 1890, 1072).

107. EILOART (*C. N.*, lviii., 284).—The calorimetric bomb suggested as a combustion-furnace.
108. SARGENT (*J. S. C. I.*, 1900, 692).—Uses a special furnace arrangement for rapid combustions. Retains Cl or HCl in column of wet sand. Modifications by JOB and DAVIS (*J. C. S.*, lxxx., ii., 127).

*c. Wet Combustion of the Residue:*

109. ELLIOT (*C. N.*, xix., 152).—Liberate C with  $\text{CuSO}_4$  and acid  $\text{CuCl}_2$ , and burn residue with  $\text{CrO}_3$  and  $\text{H}_2\text{SO}_4$ .
110. CAIRNS (*C. N.*, xxv., 271).—Oxidation with  $\text{CrO}_3$  used for graphite and for varieties of coal. See also WIESNER (*J. C. S.*, lxii., 1273).
111. PACKER (*C. N.*, xxviii., 282).—Like 109,  $\text{CO}_2$  passed through  $\text{H}_2\text{SO}_4$  into the KHO. (See 30 and 114.)
112. LANGLEY (*C. N.*, lxii., 219).—"International Standards" work. A chlorine compound passes both  $\text{Ag}_2\text{SO}_4$  and anhydrous  $\text{CuSO}_4$  into the KHO. Precautions devised.
113. PARRY and MORGAN (*C. N.*, lxvii., 175).—Liberate C with neutral and acid cuprammonium chloride. A little  $\text{CO}_2$  passes the Geissler bulb, and is retained by soda-lime (see 85).
114. SARNSTROM (*J. I. S. I.*, 1886, 1016).—The iodine carbon residue (71) is not of constant composition, and hydrocarbons are evolved during the dissolving. Hydrocarbons are evolved during combustion with  $\text{CrO}_3$ ; these are burned to  $\text{CO}_2$  with  $\text{CuO}$ .
115. GALBRAITH (*J. I. S. I.*, 1897, i., 567).—A process like Sarnström's.
116. KONINCK (*J. C. S.*, liv., 1341).— $\text{Ag}_2\text{SO}_4$  added along with the  $\text{CrO}_3$  prevents even a trace of chlorine being evolved.
117. BLUM (*C. N.*, lx., 167).— $\text{Ag}_2\text{SO}_4$  does not retain the chlorine if strong  $\text{H}_2\text{SO}_4$  is used.<sup>1</sup>
118. AUCHY (*J. S. C. I.*, 1898, 604).—The KHO should have a sp. gr. of 1.40. Occasionally chloro-chromic compounds not oxidized by Langley's "pyro" (112) are formed. In the wet combustion of graphite CO is given off.
119. AUCHY (*J. C. S.*, lxxiv., ii., 534).—The error due to condensation of moisture on the KHO bulb cannot be allowed for by using a "dummy" bulb.
120. WIDMER (*C. N.*, lxii., 274).—The C of organic bodies is not completely oxidized to  $\text{CO}_2$  by  $\text{CrO}_3$  and  $\text{H}_2\text{SO}_4$ . Some CO is formed.
121. LUDWIG (*C. N.*, xxv., 227).—CO is readily oxidized to  $\text{CO}_2$  by saturated solutions of  $\text{CrO}_3$ .
122. ALLEN (*C. N.*, lviii., 21).— $\text{CO}_2$  is always evolved on heating pure  $\text{H}_2\text{SO}_4$  and commercial  $\text{CrO}_3$ .

<sup>1</sup>Blum says, "According to Volhard,  $\text{H}_2\text{SO}_4$  diluted with half its volume of water, does not attack  $\text{AgCl}$ . This, however, is a degree of dilution which never occurs in the combustion of carbon in iron." It has since been shown that sulphuric acid, even more dilute than Volhard's, effects the combustion most rapidly. (See 125 and 128.)

123. PHELPS (*C. N.*, lxxvi., 256).—Oxidizes many organic bodies with  $\text{CrO}_3$  and after acting on Ludwig's suggestion, estimates the  $\text{CO}_2$ . Estimates the combined oxygen also, by titrating the residual  $\text{CrO}_3$ .
124. ANON. (*J. S. C. I.*, 1886, 617).—Combustion with  $\text{CrO}_3$ . Chlorine is absorbed by powdered metallic antimony.
125. LORD (*Metallurg. Anal.*, p. 62).—The proper strength of  $\text{H}_2\text{SO}_4$  in the mixture is from 50 to 70 per cent. Fused  $\text{CaCl}_2$  usually contains  $\text{CaO}$ , and so can absorb  $\text{CO}_2$  in the drying tube.
- d. Volumetric Estimation of the Carbon*—see also 19, 20, 25, etc :
126. PARRY (*C. N.*, xxv., 301).—Residue combusted with  $\text{CuO}$  in vacuum and  $\text{CO}_2$  measured. Direct combustion of Fe gives low results.
127. IMBERT and COMPAN (*C. N.*, lxxix., 267).—Carbon (lamp-black) is digested with  $\text{H}_2\text{SO}_4$  and  $\text{CrO}_3$ , and residual  $\text{CrO}_3$  estimated with  $\text{KI}$  and  $\text{Na}_2\text{S}_2\text{O}_3$ .
128. J. T. (*C. N.*, lxxx., 52 and 210).—Carbon liberated with  $\text{Cu}$  solution may be estimated by a modification of the above process, but not if  $\text{Cr}$  is present. Combined C is oxidized most rapidly by mixtures containing 50 to 70 per cent  $\text{H}_2\text{SO}_4$ , and graphite by mixtures containing 90 per cent.  $\text{H}_2\text{SO}_4$ . Mixtures of  $\text{K}_2\text{Cr}_2\text{O}_7$  containing 60 per cent. or over of  $\text{H}_2\text{SO}_4$  are slowly decomposed at  $100^\circ \text{C}$ .

#### IV. Colorimetric Estimation of Carbon.

- a. Eggertz Process and Modifications*—see also 45 :
129. EGGERTZ (*C. N.*, xliv., 173).—Desirable relation between C in steel,  $\text{HNO}_3$ , and state of dilution. Daylight bleaches colour. Comparison made in camera. Likely amounts of Mn, P, Si (see 144), S (see 134), W, Cr (see 135), Va, Ni, Co, and Cu are without influence. Permanent artificial standards. (See also 71.)
130. HERMANN (*C. N.*, xxi., 295).—Artificial standards not satisfactory. Process not suitable for high-carbon steels.
131. GREINER (*C. N.*, xx., 286).—The nitric acid solution of the steel is kept for four hours at  $80^\circ$  before comparing with the standard.
132. ROSSI (*J. I. S. I.*, 1891, i., 433).—Samples dissolved at  $80$ — $85^\circ \text{C}$ ., and the colours compared in a Duboscq colorimeter, which is described.
133. BRITTON (*C. N.*, xxvi., 139).—Use 1 grm. of material ; dissolve without heat, filter, and compare with series of standards (coffee in alcohol). Sample loses colour on standing.
134. HOGG (*C. N.*, lviii., 175).—The S of a sample is liberated as such, and has a very marked influence on the tints.
135. ZIEGLER (*J. I. S. I.*, 1890, i., 373).—Chromium gives a grey tone to Eggertz colour solution.
136. TROILIUS (*C. N.*, xliv., 292).—Compares between two standards not differing much in percentage from the sample.



137. SPULLER (*J. I. S. I.*, 1899, ii., 482).—After dissolving in  $\text{HNO}_3$ , the samples are boiled in a paraffin bath ( $135^\circ \text{C.}$ ) before comparing.
138. STEAD (*J. I. S. I.*, 1883, 213; and *C. N.*, xlvii., 285).—Dissolve 1 grm. in  $\text{HNO}_3$ , add excess  $\text{NaHO}$ , and compare filtrate with similarly treated standard steel. Moderate excess of heating,  $\text{HNO}_3$ , and  $\text{NaHO}$  are without influence.  $\text{HCl}$  must be avoided. Hardened steels give less colour.
139. HUNT (*J. I. S. I.*, 1883, 764).—The mechanical state of division of standard and sample should be alike. Stead's modification the more reliable under variable conditions. The colour is darker the more quickly the sample is dissolved. Instructions for very quick testing.
140. PARKER (*C. N.*, xlii., 88).—C exists in different conditions, so that steels containing same percentage give varying degrees of colour. The test is modified to meet this difficulty.
141. HOGG (*C. N.*, xlii., 131).—Paper on same lines as Parker's. In hardened steel there is a form of C and iron "which is decomposed by  $\text{HNO}_3$  without communicating any colour whatever."
142. HOGG (*J. I. S. I.*, 1896, ii., 179).—Classification of C existing in steel. Speculation concerning the carbon of hardened steel which evades the colour test. Eggertz colour is destroyed by continued heating and  $\text{CO}_2$  evolved. Saniter connects the missing C with the sub-carbide  $\text{Fe}_{24}\text{C}$ , Sauveur with the presence of martensite.
143. GALBRAITH (*J. I. S. I.*, 1881, 234).—Hammering, rolling, hardening, and annealing interfere with the colour test. Conditions must be strictly comparative.
144. WOODCOCK (*J. I. S. I.*, 1882, 111).—Both P and Si introduce negative errors. Carbonaceous gases are given off on dissolving hardened steel.
145. PARRY and MORGAN (*C. N.*, lxvii., 176).—Not reliable for hardened or high per cent. steels. Artificial standards no use.
146. ROBINSON (*J. I. S. I.*, 1887, ii., 363).—Artificial standards made from  $\text{CoCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{Fe}_2\text{Cl}_6$ , and  $\text{HCl}$ .
147. UKENA (*J. I. S. I.*, 1891, ii., 323).—Samples cooled in hot soapy water can be drilled as though cooled in air.

*b. Tintometers and other Apparatus :*

148. LEEDS (*C. N.*, xxxvii., 229).
149. STEAD (*J. I. S. I.*, 1883, 217; and *C. N.*, xlvii., 285).
150. RIDSDALE (*J. S. C. I.*, 1886, 585).—With some notes on Stead's modified colour process.
151. RIDSDALE (*J. S. C. I.*, 1888, 70).—A simplified apparatus for deep tints.
152. LOVIBOND (*J. S. C. I.*, 1888, 424).
153. M'MILLAN (*J. I. S. I.*, 1894, ii., 157).—Refers to previous instruments and describes two new ones.
154. KRÜSS (*J. C. S.*, lxvi., ii., 158).
155. ZANGEMEISTER (*J. C. S.*, lxx., ii., 404).

156. REDWOOD (*J. S. C. I.*, 1885, 76).  
 157. ARNOLD (*C. N.*, l., 25).—Bath of glass ; perforated lid of glazed earthenware. Tubes can be suspended any depth in the solution.  
 158. KELSALL (*C. N.*, l., 56).—A copper bath. Burnt sugar standards keep for years.

### V. Other Processes for Estimating Carbon.

159. DUPRE (*C. N.*, xxxix., 39).—Pass  $\text{CO}_2$  into solution of basic lead acetate. The cloud formed is compared with standard clouds. Very delicate.  
 160. CLERC (*J. I. S. I.*, 1885, 274).—Liberate C with  $\text{CuSO}_4$ , oxidize with  $\text{CrO}_3$ , and pass  $\text{CO}_2$  through tubes containing KHO and a little manganate. An excess of  $\text{CO}_2$  forms permanganate ; the number of tubes thus changed indicates the amount of C.  
 161. VOLMER (*J. I. S. I.*, 1895, ii., 587).—Peiper's process consists in making a metallic streak on unglazed porcelain, treating it with cuprammonium chloride, and comparing with standards.  
 162. TROPENAS and WELLS (*J. S. C. I.*, 1892, 636).—The  $\text{CO}_2$  in converter gases is proportional to the C in the metal. This  $\text{CO}_2$  is determined, and the C deduced in less than a minute. The process is patented.

### VI. Estimation of Graphite.

See also 6, 40, 71, 73, 74, 75, 76, 92, 110, 184.

163. SHIMER (*C. N.*, lxxiii., 31).—By decomposing with HCl or  $\text{H}_2\text{SO}_4$  high results are obtained due to titanium and other carbides in the residue. These carbides are easily soluble in  $\text{HNO}_3$ .  
 164. TOSH (*C. N.*, xvi., 168).—Separate Fe with HCl, and wash residue with alcohol and ether to remove hydrocarbons. In separating Si with NaHO there is always effervescence due to oxidation to silicic acid.  
 164a. DONATH and HAILSIG (*J. I. S. I.*, 1897, ii., 488).—Graphite in FeSi is determined by dissolving in  $\text{HF} + \text{H}_2\text{SO}_4$ . Combined C exists in a form analogous to carborundum. (See 232.)  
 165. EGGERTZ (*C. N.*, xviii., 232).—Decompose with  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , evaporate, and re-dissolve in HCl. Dry filtered graphite and  $\text{SiO}_2$  on tared filter at  $100^\circ \text{C}$ . Loss on ignition = graphite.  
 166. PIESSE (*C. N.*, xxix., 57).—Very much like 165. Dries at  $212^\circ$ .  
 167. ALLEN (*C. N.*, xxix., 91).—Criticism of Piesse's paper. Dissolve in HCl. Silicon and carbon compounds removed with KHO, and graphite determined by loss on ignition of the strongly dried residue.  
 168. MACKINTOSH (*C. N.*, li., 147).—To estimate graphite in minerals, fuse with KHO, wash residue with HCl, etc., dry, and weigh.  
 169. HOCK (*J. I. S. I.*, 1882, 324).—Ignite residue under charcoal cover in a tared crucible ; weigh, ignite, and determine graphite by loss. Ignite

- the separated filter-paper, and from the residue calculated the graphite which adhered to the paper according to the ratio  $\frac{\text{graphite}}{\text{ash}}$  established by the burning of the bulk of the graphite.
170. CROBAUGH (*J. I. S. I.*, 1894, ii., 488).—Collect on counterpoised filters; remove  $\text{SiO}_2$  with HF and  $\text{HNO}_3$ ; digest with  $(\text{NH}_4)\text{HO}$  to remove carbonaceous compounds.
  171. TAMM (*J. I. S. I.*, 1887, ii., 361).—Dries separated graphite at  $100^\circ$ , and divides residue, after ignition, by 0.94 to allow for water in  $\text{SiO}_2$ . See also FORD and BREGOWSKY (*J. C. S.*, lxxviii., ii., 168).
  172. AUCHY (*J. S. C. I.*, 1900, 276).—Graphite as prepared for estimation by loss on ignition may contain H, O, N, and S.
  173. PARRY (*C. N.*, lxvii., 247).—Separate Fe with HCl, wash residue with KHO, alcohol, and ether; mix with CuO and burn in O, or dry on weighed paper at  $100\text{--}120^\circ\text{C}$ .
  174. STOLBA (*J. S. C. I.*, 1888, 235).—The combustion of graphite is promoted by mixing with silver dust.
  175. WIDMER (*J. C. S.*, lviii., 923).—Cross and Bevan's observation that with  $\text{CrO}_3$  part of the C is gasified as CO is true for graphite. To avoid error (5 per cent.) the gases are passed over CuO.
  176. SHIMER (*C. N.*, lv., 231).—To sample graphitic irons moisten borings with alcohol, remove a portion, dry and weigh. (See also *J. I. S. I.*, 1889, ii., 472).

## VII. Miscellaneous Notes.

177. WARREN (*C. N.*, xiv., 85).—An interesting account of the combustion of organic bodies in oxygen.
178. BERTHELOT (*C. N.*, xix., 113).—"Immediate Analysis of Different Varieties of Carbon."
179. LEDEBUR (*C. N.*, xlvii., 107).—To remove grease from the sample ignite in a current of dry nitrogen.
180. RAWSON (*C. N.*, xlix., 161).—"The Estimation of Cuprous Chloride in Copper Liquors."
181. DONALD (*C. N.*, lxiii., 73).—By rusting, pig-iron drillings lose a portion of their graphite.
182. LEEDS (*J. I. S. I.*, 1881, 658).—"Burnt" steel contains the same amount of C as the same steel before burning.
183. HEMPEL (*C. N.*, lxix., 277).—Processes for estimating C classified and criticised. Ullgren (109), Weyl (32), and Wöhler's (77) processes preferred.
184. LEDEBUR (*J. I. S. I.*, 1894, i., 603).—Direct combustion of grey pig gives low results. Juptner's method (17) gives low results, due to escape of hydrocarbons. With Sarnström's modification (114) the results are accurate. Similar remarks apply to wet combustion of the C residue. Removal of Fe by cuprammonium chloride unsatisfactory. Separa-

- tion of Fe with Cl most accurate if well done.  $\text{HNO}_3$  preferable to  $\text{HCl}$  for separating Fe and graphite.
185. GÖTTIG (*J. I. S. I.*, 1894, i., 607).—Dry direct combustion inaccurate. Juptner's process (17) available if much  $\text{CrO}_3$  is used. Cu and C need not be separated for wet combustion; must be for dry. Processes separating the iron and burning the residue in the dry way are inaccurate.
  186. DOUGHERTY (*J. I. S. I.*, 1897, i., 573).—In FeSi compounds determines Fe, Si, Mn, S, and P, and then calculates the carbon by difference. (See 164a.)
  187. TABARY (*J. I. S. I.*, 1895, i., 492).—Irregular distribution of carbon in pig-iron.
  188. LUZI (*J. I. S. I.*, 1893, ii., 334).—Graphite, so-called, may contain "graphitite" also. They behave differently with nitric acid.
  189. LEDEBUR (*J. I. S. I.*, 1889, i., 368; and 1893, ii., 53).—Distinguishes hardening C, carbide C, graphitic temper C, and graphite; their properties and means of estimating them. (See also 8.)
  190. LEDEBUR (*J. I. S. I.*, 1891, i., 364).—Analysis of variously treated irons and steels, including graphite, graphitic temper carbon, hardening carbon, and carbide carbon.
  191. JUPTNER (*J. I. S. I.*, 1897, i., 248).—Estimates hardening and carbide C by a modification of the colour test. Summary of Osmond and Werth's investigation of the colour test. Graphite is oxidized on boiling with  $\text{HNO}_3$ . Bamber (p. 266) vigorously criticises the methods. (See also p. 554.)
  192. DIXON (*J. C. S.*, lxi., 774).—"Mode of Formation of  $\text{CO}_2$  in the Burning of Carbon Compounds."
  193. ABEL and DEERING (*C. N.*, xlvii., 200).—Carbon exists in cold rolled steel as  $\text{Fe}_3\text{C}$ . It is separated with a dilute solution of  $\text{CrO}_3$  and  $\text{H}_2\text{SO}_4$ . See also MULLER (*J. I. S. I.*, 1888, ii., 295, and 1895, i., 495), ARNOLD and READ (*J. C. S.*, lxxv., 788), and MYLIUS, FOERSTER, and SCHOENE (*J. C. S.*, lxxii., ii., 39).

**SILICON.**

The items are arranged, as sharply as possible, under the following heads :

**I. THE ESTIMATION OF SILICON IN METALS.**

- a.* Iron and Steel.
- b.* Alloys.
- c.* Aluminium.

**II. THE ESTIMATION OF SILICA IN REFRACTORY MATERIALS.****III. THE ESTIMATION OF SILICA IN SLAGS AND SILICATES.****IV. MISCELLANEOUS.****I. The Estimation of Silicon in Metals.***a. In Iron and Steel :*

194. ABEL (*C. N.*, vi., 124); and FORBES (*C. N.*, xvi., 105).—Pig dissolved in HCl, evaporated; Si dissolved from the graphite with KHO, and recovered again by evaporation with HCl.
195. ALLEN (*C. N.*, xxix., 91).—Similar to Abel. When iron is dissolved in HCl or H<sub>2</sub>SO<sub>4</sub>, the silicon is liberated not as SiO<sub>2</sub>, but as leucon. (See also 164 and SCHAFHAUTL, *C. N.*, iv., 165.) For particulars of leucon see WÖHLER (*C. N.*, viii., 171 and 182, and BRADLEY, *C. N.*, lxxxii., 150).
196. SCHNEIDER (*J. C. S.*, lxvi., ii., 162).—Dissolve in HCl, and evaporate with H<sub>2</sub>SO<sub>4</sub> to dehydrate the silica.
197. BLUM (*C. N.*, liii., 300).—Dissolve in HCl and evaporate. The addition of (NH<sub>4</sub>)Cl increases the rapidity of evaporation.
198. RUBRICIUS (*J. I. S. I.*, 1893, i., 411).—Dissolve pig in small excess of HCl, filter at once, ignite residue with KNO<sub>3</sub>, boil with (NH<sub>4</sub>)Cl, and collect the hydrated silica.
199. SCHNEIDER (*J. I. S. I.*, 1893, ii., 532).—Processes of evaporation with HCl, or solution of the baked residue in HCl, are erroneous. SiO<sub>2</sub> is markedly soluble in HCl: it should be dehydrated by evaporation with H<sub>2</sub>SO<sub>4</sub>.
200. DROWN (*C. N.*, xlii., 299).—On dissolving Fe in HCl, the less Si passes into solution the stronger the acid. High Si irons may be fused with KHSO<sub>4</sub>, digested with HCl, and SiO<sub>2</sub> filtered off.
201. ALLEN (*C. N.*, xl., 65).—As leucon, the form in which Si is liberated from iron, is soluble in water, no fixed proportion of silicon invariably passes into solution. Means of distinguishing leucon given.
202. EGGERTZ (*C. N.*, xvii., 100 and 115).—Dissolve Fe with Br or I and water at 0° C., and separate SiO<sub>2</sub> from the slag with Na<sub>2</sub>CO<sub>3</sub>Aq. If iron is dissolved in HCl, very little Si passes into solution; if HNO<sub>3</sub>, much. By dissolving in H<sub>2</sub>SO<sub>4</sub>, and evaporating to SO<sub>3</sub> fumes, nearly all the SiO<sub>2</sub> is separated.

203. EGGERTZ (*C. N.*, xviii., 232).—Dissolve in  $\text{H}_2\text{SO}_4$  ; add  $\text{HNO}_3$ , evaporate, re-dissolve in  $\text{HCl}$ , and collect  $\text{SiO}_2$ .
204. PIESSE (*C. N.*, xxix., 57).—Effect solution with nitro-sulphuric acid and evaporate at  $100^\circ \text{C}$ .
205. DROWN (*C. N.*, xl., 40).—Decompose with nitro-sulphuric acid and evaporate to  $\text{SO}_3$  fumes. By treating iron with  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HNO}_3$ , the Si passing into solution is in the order named.
206. DROWN (*C. N.*, lx., 20).—Nitric acid of sp. gr. 1.135 dissolves pig-iron completely without causing any  $\text{SiO}_2$  to separate.
207. LANGMUIR (*C. N.*, lxxix., 216).—To effect a more complete dehydration in (205) a strap is passed round the beaker, and the solution kept in motion over the naked flame.
208. JONES (*C. N.*, lx., 79).—The nitro-sulphuric acid solution is evaporated in three to five minutes by two flames, one of which impinges on the surface of the liquid.
209. AUCHY (*J. I. S. I.*, 1898, ii., 559) ; and CROBAUGH (*J. I. S. I.*, 1899, ii., 484).—To use a mixture of aqua regia and  $\text{H}_2\text{SO}_4$  is more accurate and convenient than nitro-sulphuric acid. See also Reis (*J. I. S. I.*, 1888, 373).
210. JÜPTNER (*J. I. S. I.*, 1884, 603).—Comparison of various methods. Drown's process (205) gives good results in the presence of Ti. Estimating  $\text{SiO}_2$  by volatilization with  $\text{HF}$  is objectionable.
211. DUDLEY (*C. N.*, lxx., 186).—Silica dehydrated by evaporation to  $\text{SO}_3$  fumes is partially re-dissolved when allowed to stand in the acid solution.
212. FORD (*J. S. C. I.*, 1893, 1061).—Silica dehydrated by process 205 is not re-dissolved as Dudley suggests.
213. JERVIS (*C. N.*, lxxviii., 63).—Dissolve in dilute nitro-sulphuric acid, and deliver water on to the dry hot mass ; this avoids cooling cracks, and no  $\text{SiO}_2$  is re-dissolved on standing.
214. TROILIUS (*C. N.*, xlv., 310).—Dissolve in dilute  $\text{H}_2\text{SO}_4$ , evaporate to  $\text{SO}_3$ , dissolve separated salt in  $\text{HCl}$ , filter off  $\text{SiO}_2$ , and wash with  $\text{HNO}_3$ .
215. TURNER (*C. N.*, lvi., 49).—Phosphoric irons evaporated with  $\text{H}_2\text{SO}_4$  may give a white, but still impure,  $\text{SiO}_2$ . When evaporated with aqua regia, the colour of the  $\text{SiO}_2$  is an indication of purity.
216. TOSH (*C. N.*, xvi., 168).—Evaporate aqua regia solution, fuse  $\text{SiO}_2$  with  $\text{KNO}_3$ , and evaporate the dissolved melt with  $\text{HCl}$ .
217. MORGAN (*C. N.*, lvi., 221 and 244).—Evaporate aqua regia solution to syrupy condition only ; the  $\text{SiO}_2$  from highly phosphatic irons is free from phosphide of iron.
218. PARRY and MORGAN (*C. N.*, lxvii., 149).—As Morgan ; but evaporate to dryness and then re-evaporate  $\text{HCl}$  solution to skin ; fuse with  $\text{KHSO}_4$ , to separate iron phosphide.  $\text{H}_2\text{SO}_4$  is essential when  $\text{SiO}_2$  is to be volatilized with  $\text{HF}$ .

219. LIEBRICH (*J. I. S. I.*, 1896, i., 532).—After evaporating acid solution of the pig, ignite the filtered residue with  $\text{KHSO}_4$  to burn off graphite and separate Fe and Ti.
220. LECLERC (*J. C. S.*, lx., 1397).—Dissolve in nitro-hydrochloric acid, expel  $\text{HNO}_3$ , and evaporate after addition of ammonium chloride to prevent Mn contaminating  $\text{SiO}_2$ , and KCl to prevent the decomposition of  $\text{Fe}_2\text{Cl}_6$ .
221. TURNER (*J. C. S.*, xlv., 260).—Various methods compared. Dissolving in HCl or  $\text{HNO}_3 + \text{H}_2\text{SO}_4$  untrustworthy for Si pigs or Si spiegels.
222. MORGAN (*C. N.*, lvi., 83).—Roast finely-divided sample in the muffle to oxidize Si, digest with HCl, and collect  $\text{SiO}_2$ .
223. WATTS (*C. N.*, xlv., 279); and TURNER (*C. N.*, xlix., 233).—Volatilize Si along with iron in Cl at red heat, collect  $\text{SiCl}_4$  in  $\text{H}_2\text{O}$ , and evaporate for  $\text{SiO}_2$ . Any slag or cinder remains with the carbon in the boat. (See 202 and 281.)
224. KONINCK (*J. I. S. I.*, 1894, i., 614).—The solution of the iron is precipitated by  $(\text{NH}_4)\text{HO}$  or acetate, and the ignited precipitate heated in HCl gas;  $\text{SiO}_2$  (and  $\text{Al}_2\text{O}_3$ ) remain in the boat.

*b. In Alloys:*

225. CLERC (*J. I. S. I.*, 1889, ii., 479).—Dissolve powdered ferro-silicon in bromized HCl, evaporate one-half, and collect  $\text{SiO}_2$ ; the error is insignificant.
226. HOGG (*C. N.*, lxvii., 27).—Boiled finely-powdered Fe-Si or Si spiegel with nitro-hydrochloric acid, filter, and ignite to  $\text{SiO}_2$ . Only 0.1 to 0.3 per cent. Si passes into solution when dealing with 10 to 15 per cent. alloys.
227. PLATT (*J. I. S. I.*, 1893, i., 411).—As Hogg, but adds  $\text{H}_2\text{SO}_4$  containing  $\text{SO}_3$  to render Si insoluble.
228. MURRAY and MAURY (*J. C. S.*, lxxii., ii., 599).—Decompose silico-spiegel with  $\text{HCl} + \text{H}_2\text{SO}_4$ , evaporate to  $\text{SO}_3$  fumes, and volatilize  $\text{SiO}_2$  with HF. Done in half an hour.
229. WILLIAMS (*J. I. S. I.*, 1889, i., 397).—Fuse Fe-Si with  $\text{Na}_2\text{CO}_3$  and evaporate melt with HCl; the  $\text{SiO}_2$  is pure.
230. ZIEGLER (*C. N.*, lxvi., 295).—Fuse Fe-Si or Fe-Cr with  $\text{KHSO}_4$ , dissolve melt, and collect  $\text{SiO}_2$ .
231. DONATH and HAILSIG (*J. I. S. I.*, 1897, ii., 488).—Ferro-silicons cannot be dissolved by HCl,  $\text{HNO}_3$ , or aqua regia. Fuse with  $\text{Na}_2\text{CO}_3$  and  $\text{NaNO}_3$ .
232. IBBOTSON and BREARLEY (*C. N.*, lxxxii., 269).—Estimation of combined and graphitic carbon, Si, Mn, and P in FeSi alloys.
233. GRAY (*J. S. C. I.*, 1901, 538).—Ca occurs in high-grade FeSi. Mode of analysing such alloys after decomposing with carbonates.
234. JOUVE (*C. N.*, lxxxiii., 182).—Explains how Si exists in commercial FeSi alloys. Also Lebeau (*J. C. S.*, lxxx., ii., 317).

235. NEWMANN (*J. S. C. I.*, 1900, 1146).—Estimation of the various impurities in commercial silicon and their mode of occurrence.
236. BORINTRAGER (*J. C. S.*, lxxvi., ii., 695).—Silicon is analysed by dissolving in potash; the impurities,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and Fe-Si are left undissolved.
237. TATE (*C. N.*, lxxx., 235).—Fuse FeCr with  $\text{Na}_2\text{O}_2$ , evaporate the neutralized melt, and heat with  $\text{H}_2\text{SO}_4$  to fuming; finally, vaporize  $\text{SiO}_2$  with HF. Much of the Cr escapes during the  $\text{H}_2\text{SO}_4$  treatment as chlorochromic acid.
238. MOISSAN (*J. C. S.*, lxvi., ii., 43).—Carbide of silicon (carborundum) is decomposed by fusion with KHO.  $\text{KNO}_3$  and  $\text{KClO}_3$  have no effect on it, nor has any mixture of acids.
239. MUHLHAEUSER (*J. S. C. I.*, 1894, 402).—Uses the elutriated powder of carborundum, and decomposes with KNaHO. Estimates the carbon by burning a like powder with  $\text{PbCrO}_4$ .
240. SCHUTZENBERGER (*J. C. S.*, lxii., 1050).—Carborundum as Moissan. The volatilization of the Si in a current of chlorine is not complete.

*c. In Aluminium:*

241. HUNT, CLAPP, and HANDY (*C. N.*, lxx., 223).—Si exists in Al in the graphitoidal and combined form. Dissolve in nitro-hydrochloric acid, evaporate with  $\text{H}_2\text{SO}_4$ , and collect Si +  $\text{SiO}_2$ .  $\text{SiO}_2$  cannot be estimated by volatilization; Si is also partially oxidized, therefore fuse with  $\text{Na}_2\text{CO}_3$ , dissolve in HCl, evaporate with  $\text{H}_2\text{SO}_4$ , and weigh total Si as  $\text{SiO}_2$ .
242. HANDY (*J. C. S.*, lxxii., ii., 191).—To determine graphitic Si decompose Al with  $\text{HCl} + \text{HF}$ , filter through paraffin-coated funnel, fuse with  $\text{Na}_2\text{CO}_3$ , and estimate as  $\text{SiO}_2$ .
243. REGELSBERGER (*J. C. S.*, lxiv., ii., 48).—Decompose with aqua regia +  $\text{H}_2\text{SO}_4$ , drive off  $\text{HNO}_3$ , collect Si +  $\text{SiO}_2$ , and evaporate with HF; loss =  $\text{SiO}_2$ . Evaporate residue with  $\text{HF} + \text{HNO}_3$ ; loss of weight = Si. (See 241 and 294.)
244. MOISSAN (*J. C. S.*, lxx., ii., 339).—Decompose with HCl, fuse insoluble and add to main solution; evaporate at  $125^\circ \text{C}$ . to separate  $\text{SiO}_2$ .
245. SIBBERS (*J. C. S.*, lxxiv., ii., 409).—On dissolving Al in HCl appreciable amounts of Si are volatilized. Dissolve in current of H, which on ignition at the delivery tube deposits  $\text{SiO}_2$ .
246. GONTHIERE (*J. S. C. I.*, 1896, 83).—Dissolves in nitro-hydrochloric acid and proceeds as for steels, taking no account of graphitic Si.
247. SCHWEIZ (*J. S. C. I.*, 1892, 548).—Dissolve in KHO, acidulate with HCl, evaporate, and collect  $\text{SiO}_2$ .

## II. The Estimation of Silica in Refractory Materials.

248. CAMERON (*C. N.*, lxix., 171).—After fusion all evaporations should be made with HCl not  $\text{H}_2\text{SO}_4$ . (See 274.) One evaporation does not



make all the  $\text{SiO}_2$  insoluble. The influence exerted by Fe, Al, Ca, and organic matter is observed.

249. CRAIG (*C. N.*, lx., 227).—On account of imperfect dehydration of  $\text{SiO}_2$  and contamination of precipitates with sodium salts, fusion is undesirable. Drive off  $\text{SiO}_2$  with HF and  $\text{H}_2\text{SO}_4$ . A simple apparatus for purifying HF. (See 269.)
250. ARCHBUTT (*J. S. C. I.*, 1892, 215).—Confirms 249. The  $\text{SiO}_2$  of clays is not completely insoluble after  $\text{KHSO}_4$  fusion. Filtrates evaporated with  $\text{H}_2\text{SO}_4$ .
251. ROCHOLL (*C. N.*, xli., 234).—Limestones, siliceous ores, and like minerals are readily decomposable with HCl after strong ignition; the bases already present acting as flux.
252. KERN (*C. N.*, xxxv., 203).—A process for the estimation of  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , MnO, CaO, and MgO in fire-clay, etc. Opens out by  $\text{Na}_2\text{CO}_3$  fusion.
253. ANON. (*C. N.*, v., 228).—Comparative value of fire-bricks determined by heating simultaneously under layer of limestone and observing the degree to which they have been acted upon.

### III. The Estimation of Silica in Slags and Silicates.

254. ROSE (*C. N.*, i., 179).—Silicates may be decomposed by heating with powdered ammonium fluoride. Also HOFFMAN (*C. N.*, xvii., 94).
255. AVERY (*C. N.*, xix., 270).—Almost any acid with a normal fluoride will completely dissolve silicates; the loss of  $\text{SiO}_2$  need only be very slight.
256. KUHLMANN (*C. N.*, xi., 194).—Silicates decomposed in current of HF at dull redness. Necessary apparatus described.
257. STORY-MASKELYNE (*C. N.*, xxi., 27).—Decompose silicate in a special form of platinum apparatus, collect volatile  $\text{SiO}_2$  in ammonia, precipitate the neutral solution with KCl and alcohol, and weigh as fluo-silicate.
258. ALLEN (*J. C. S.*, lxx., 575).—A small crucible containing the powdered silicate moistened with  $\text{H}_2\text{SO}_4$  is placed in a larger one containing  $\text{H}_2\text{SO}_4 + \text{HF}$ . A dish of cold water placed over the larger crucible causes re-distilled HF to drop into the smaller. (See 249.)
259. FELLEBERG (*C. N.*, xiv., 243).—Fuse with  $\text{CaCl}_2 + \text{CaO}$ , leach with water; the solution contains only Ca and the alkalis.
260. GLINKA (*J. C. S.*, lxiv., ii., 491).—Fuse with  $\text{CaCO}_3$ , decompose melt with nitro-hydrochloric acid, and proceed as usual.
261. BONG (*C. N.*, xxxvii., 112).—Silicates are completely decomposed by fusion with  $\text{Pb}_3\text{O}_4$  at low temperatures. Dissolve melt in  $\text{HNO}_3$ , and evaporate for  $\text{SiO}_2$ .
262. JANNASCH (*C. N.*, lxxii., 51).—As BONG, but uses lead carbonate.

263. LECLERC (*C. N.*, lxxvii., 27).—As BONG, but does not appear to evaporate before filtering off the “completely insoluble hydrated silica.”
264. HEMPEL (*C. N.*, xlv., 81).—Fuse silicate with subnitrate of bismuth, dissolve in HCl, and evaporate for SiO<sub>2</sub>.
265. CHATARD (*C. N.*, l., 279).—As Hempel, but uses the oxide.
266. ILES (*C. N.*, xliii., 78).—Decompose by fusion with KHO in Ag crucible. The SiO<sub>2</sub> is washed with ammonia to remove AgCl. (See 1279.)
267. HOLTHOP (*C. N.*, li., 18).—Fuse with NaHCO<sub>3</sub>. At the moment of formation of the normal carbonate the base has an intensified affinity for SiO<sub>2</sub>.
268. SHIMER (*C. N.*, lxx., 102).—Spinel (magnesium aluminate), which may occur in blast-furnace slags, is not decomposed by alkaline fusion nor with HF + H<sub>2</sub>SO<sub>4</sub>; it is by KHSO<sub>4</sub>. (See 274.)
269. GILBERT (*C. N.*, lxi., 270 and 281).—Evaporation of fusion with HCl does not make all the SiO<sub>2</sub> insoluble. CaCl<sub>2</sub> assists dehydration, but neither CaO nor Al<sub>2</sub>O<sub>3</sub> tends to re-form silicates at higher temperatures; MgO does. (See 290.)
270. LINDO (*C. N.*, l., 25).—The character of the SiO<sub>2</sub> may be vitreous or amorphous, according to the varying treatment of the alkaline melt with acids.
271. ILES (*C. N.*, l., 194).—Hot slags plunged into cold water are completely decomposed by HCl. Complete analysis of slags; lime is determined in the presence of the iron.
272. JONES (*J. I. S. I.*, 1888, i., 383).—Compares the fusion process and dissolving of chilled (271) samples in HCl. Dehydrates SiO<sub>2</sub> in either case at 120° C.
273. CAMP (*J. I. S. I.*, 1897, i., 578).—Decompose blast-furnace slags with HCl, and evaporate twice for SiO<sub>2</sub>.
274. MEEKER (*J. S. C. I.*, 1897, 636).—H<sub>2</sub>SO<sub>4</sub> dehydrates better than HCl evaporation, but the filtrate cannot be used for the estimation of Ca and Al. Yields good results in the presence of spinel (268).
275. JANNASCH (*J. C. S.*, lxx., 576 and *C. N.*, lxxxii., 131).—Fuse with boric acid. Boric acid eliminated by evaporation with HCl and methyl alcohol.
276. JANNASCH (*J. S. C.*, lx., 619).—Decomposed by heating with HCl in sealed tubes.
277. WINKLER (*C. N.*, i., 215).—Pyrogenous silicates in fine powder are dissolved by alcohol saturated with HCl.
278. HUTCHINGS (*C. N.*, liv., 173).—A neat qualitative analysis of silicates, chiefly by means of the blowpipe.
279. FRIEDBURG (*C. N.*, lxii., 22).—A complete analysis (Si, Fe, Al, Mn, Ca, Mg, Ba, Sr, alkalis, H<sub>2</sub>O, P, F, and Ti) of insoluble silicates.
280. HILLEBRAND (*C. N.*, lxxviii., 43, and lxxxiii., 66, etc.).—A lengthy review of the analysis of silicate rocks, paying much attention to the elements occurring in small amounts.

## IV. Miscellaneous.

281. BARROWS and TURNER (*J. C. S.*, lxi., 551).—Volatilization of the iron with Cl is not suited to the estimation of slag containing iron compounds; the sample should be decomposed by cupra-sodium chloride. (See 202 and 223.)
- 281a. SCHNEIDER (*J. I. S. I.*, 1900, ii., 577).—Critical examination and resumé of the modes of estimating slag in irons.
282. THOMAS (*J. I. S. I.*, 1888, ii., 241).—The percentage of Si in a pig varies; it is higher at the point of a pig than at the butt.
283. PHIPSON (*C. N.*, xi., 278).—Si exists in iron in two states, distinguished by their behaviour with aqua regia.
284. TOSH (*C. N.*, xiii., 145, 178, and 217).—Discredits the existence of Phipson's graphitic silicon, and also the later statement that the two forms are the silicide and silicate.
285. HOGG (*J. S. C. I.*, 1895, 245 and 262).—Is Si capable of existing in two conditions analogous to that of C in the hardened and annealed steels?
286. MORTON (*C. N.*, xxix., 107).—Experiments showing that Si exists in pigs as a silicide of iron. Also JORDON and TURNER (*J. C. S.*, xlix., 215).
287. CARNOT and GOUTAL (*J. C. S.*, lxxii., ii., 555).—Si exists in iron as silicides intermediate between  $\text{Fe}_3\text{Si}_2$  and  $\text{Fe}_5\text{Si}_3$ , but it combines with Mn in preference to iron.
288. SKEY (*C. N.*, xvi., 187).— $\text{SiO}_2$  thrown down by evaporation with HCl can retain small amounts of P.
289. HAUTEFEUILLE (*C. N.*, l., 272).— $\text{SiO}_2$  should not be dehydrated in the presence of phosphoric acid above  $100^\circ \text{C}$ .
290. LORD (*Metall. Anal.*, p. 13).—In the presence of  $\text{CaCl}_2$  dehydrate  $\text{SiO}_2$  at  $100^\circ \text{C}$ ; higher temperatures may cause the  $\text{SiO}_2$  to re-combine with the bases. (See 269.)
291. LAUFER (*C. N.*, xxxvii., 162).—By melting a silicate with a salt of P, the metallic oxides are dissolved, but not the quartz; separate amorphous  $\text{SiO}_2$  with NaHO.
292. LUNGE (*J. S. C. I.*, 1897, 762).—Aqueous soda attacks quartz;  $\text{Na}_2\text{CO}_3$  is better for separating amorphous silica.
293. MICHAELIS (*J. S. C. I.*, 1895, 1065).—Boiling ten per cent  $\text{Na}_2\text{O}$  does not attack quartz. Quartz in clay is often so finely divided as to pass through filter-paper.
294. CARON (*C. N.*, v. 102).—The only acids which attack crystallized silicon are a mixture of nitric and hydrofluoric.
295. NEWTH (*J. S. C. I.*, 1895, 1074).—Crystallized Si burns in HF gas at a moderate temperature.
296. FRESSENIUS and HINTZ (*C. N.*, lx., 85).—Cryolite is analysed by heating with  $\text{H}_2\text{SO}_4$  in a leaden tube; the volatile fluorides are absorbed in

ammonia. For other means of estimating Si when F is present see HAMPE (*J. C. S.*, lxii., 1127), REICH (*J. C. S.*, lxx., 531), and STAHL (*J. C. S.*, lxx., 621).

297. HIRSCHWALD (*C. N.*, lxii., 24).—Microcosmic fusion is of doubtful analytical significance, because  $\text{SiO}_2$  is appreciably soluble in the bead of the double salt.

## MANGANESE.

The following classification is adopted :

- I. SEPARATING THE IRON.
  - a. Precipitating the Iron.
    1. As Acetate. 2. Sulphate. 3. Hydrate. 4. Other Reagents.
  - b. Precipitating the Manganese.
- II. SEPARATING OTHER ELEMENTS.
- III. GRAVIMETRIC ESTIMATION OF MANGANESE.
  - a. As Mangano-manganic Oxide.
  - b. As Manganese Pyrophosphate.
  - c. As Manganese Sulphate.
  - d. As Manganese Sulphide.
  - e. As Manganese Carbonate.
  - f. Electrolytically.
  - g. Miscellaneous.
- IV. VOLUMETRIC ESTIMATION OF MANGANESE.
  - a. Titrations with Standard Permanganate.
  - b. Oxidations to Permanganate.
  - c. Oxidations to Higher Oxides of Manganese.
    1. The Chlorate Process.
    2. Other Oxidimetric Processes.
    3. Available Oxygen in Ores, etc.
  - d. Indirect Processes.
  - e. Miscellaneous Processes.
- V. DETECTION OF MANGANESE.
- VI. MISCELLANEOUS NOTES.

### I. Separation of Iron.

- a. 1. *Precipitating the Iron with Acetate (Succinate or Formate).* See also Nickel Bibliography.
298. KESSLER (*C. N.*, xxvii., 14).—Explains the state of a solution of ferric chloride when sodium carbonate is added to faint precipitation. Imper-

fect separations are due to excess of acetate ; a minimum quantity stated.

299. ROSENTHAL (*C. N.*, xxxvi., 147).—A re-precipitation by the acetate process is quite unnecessary.
300. JEWETT (*C. N.*, lx., 273).—Five per cent free acetic acid causes complete separation when large amounts of sodium acetate are used. The same is true for zinc and nearly so for Ni and Co.
301. MEINECKE (*J. C. S.*, lvi., 309).—The successful separation depends on perfect neutralization, small amounts of acetate and acetic acid, and short rapid boiling.
302. BREARLEY (*C. N.*, lxxv., 13).—Free acetic acid corrects errors due to large excesses of acetate. Separations complete with one precipitation without free acetic if small amount of acetate is used.
303. RIGGS (*J. C. S.*, lxii. 536).—There is a danger of a little Mn separating as higher oxide when the solution is neutralized previous to acetate separation.
304. TAMM (*C. N.*, xxvi., 37).—Precipitates with succinates. Objects to oxidation of iron with  $\text{HNO}_3$ , because part of the Mn is then always in  $\text{Mn}_2\text{O}_3$  state and precipitated with the Fe ; recommends  $\text{KClO}_3$ , or evaporation of  $\text{HNO}_3$  entirely.
305. FRESSENIUS (*Quant. Anal.*).—Basic formates are more easily washed than acetates. Succinates are said to completely precipitate Al along with the Fe.

*a. 2. Precipitating the Iron with Sulphates :*

306. KESSLER (*J. I. S. I.*, 1880, 353).—Mixed chlorides are thoroughly neutralized with  $\text{Na}_2\text{CO}_3$  ; the diluted solution is precipitated in the cold with  $\text{Na}_2\text{SO}_4$ , and straightway filtered. (A translation of this paper appears in *Iron*, May 31, 1879.)
307. MEINECKE (*J. C. S.*, lvi., 310).—Precipitates with  $(\text{NH}_4)_2\text{SO}_4$  at ordinary temperatures. Mn, Ni, Co, Cu, and Zn are in solution, and Al partly. (See 1121.)
308. RUPP (*J. I. S. I.*, 1896, i., 535).—Solution neutral, but no definite precipitate ; 18 c.c. 10 per cent.  $\text{Na}_2\text{SO}_4$  precipitates 4 grms. Fe in the cold ; filtrate titrated with permanganate.

*a. 3. Precipitating the Iron as Hydrate :*

309. SARNSTROM (*C. N.*, xlvii., 177).—Preparatory to estimating the Mn by Guyard's process, the Fe is precipitated by a small excess of sodium bicarbonate. (See 411, 412, and 413.)
310. MEINECKE (*J. I. S. I.*, 1888, ii., 326).—Fe solution saturated with  $\text{CO}_2$ , neutralized with sodium bicarbonate, and carefully coagulated with a drop more. Precipitate free from Mn, Co, and Ni. Process not available in presence of much Al. Phosphate method of precipitating Fe worthless ; precipitation with  $\text{HgO}$  of little use ;  $\text{BaCO}_3$  always leaves

Mn in precipitate. See also *J. C. S.*, lvi., 310, for separation of other elements by a similar process.

311. **FRESENIUS** (*Quant. Anal.*, p. 437, 7th ed.).—Add ammonium carbonate so that fluid loses its transparency and tends to become more turbid rather than otherwise, then boil; the iron is precipitated. Described also by Dittmar (*Quant. Anal.*, p. 74). Known as Schwarzenberg or Herschell's method.

*a. 4. Iron Precipitated by various Reagents:*

312. **Zinc Oxide**.—VOLHARD (*C. N.*, xl., 207; *J. I. S. I.*, 1880, 355).—Dilute  $\text{H}_2\text{SO}_4$  solution of the metals neutralized with soda carbonate; emulsion of ZnO added until complete precipitation of Fe is indicated by sudden coagulation of the solution.
313. **Ammonium Chloride**.—KERN (*C. N.*, xxxiii., 90).— $\text{Fe}_2\text{Cl}_6 + \text{MnCl}_2$  precipitated with KHO, large amount  $(\text{NH}_4)\text{Cl}$  added and boiled; the filtrate contains the Mn. It is further precipitated as sulphide and estimated as sulphate.
- 313a. KERN (*C. N.*, xxxv., 270).—Powdered sample mixed with  $(\text{NH}_4)\text{Cl}$  and strongly ignited; process repeated until Fe is volatilized. Residue separated from  $\text{SiO}_2$ , etc., is weighed as  $\text{Mn}_3\text{O}_4$ . (See 364.)
314. **Barium Carbonate**.—FORBES (*C. N.*, xvi., 105), and JUPTNER (*J. I. S. I.*, 1885, i., 247), separate Fe with  $\text{BaCO}_3$ . (See 310.)
315. **Sodium Phosphate**.—BLOXAM (*C. N.*, l., 112).—Speaks unfavourably of the acetate process. Precipitates neutralized iron solution with ammonium acetate and excess of sodium phosphate; ferric phosphate re-dissolved and re-precipitated; Mn in filtrate estimated as  $\text{Mn}_2\text{P}_2\text{O}_7$ . (See 310.)
316. **Chlorine**.—KERN (*C. N.*, xxxv., 247).—Precipitate Fe and Mn together with ammonia. Volatilize Fe in current of Cl; estimate residue as  $\text{Mn}_3\text{O}_4$ .
317. FRIEDMANN (*J. I. S. I.*, 1888, ii., 328).—Volatilize Fe in Cl. Graphite, Cu, Co, Ni, Mn, and slag in the residue.
318. **Sulphuretted Hydrogen**.—CARNOT (*J. I. S. I.*, 1887, i., 470).—Acetate added to neutralized solution and  $\text{H}_2\text{S}$  passed through; Fe, Ni, and Co are completely precipitated.
319. **Lead Carbonate**.—CAMPBELL (*J. C. S.*, lxii., ii., 103).—Ferric solutions are precipitated by  $\text{PbCO}_3$ . Mn, Co, Ni, and ferrous salts are not decomposed. Warming assists the reaction; nitrates should be absent.
320. **Lead Oxide**.—FIELD (*C. N.*, i., 4).—Mn, Ni, and Co are separated from Fe by precipitating with this reagent.
321. **Sodium Nitrite**.—WYNKOOP (*J. C. S.*, lxxiv., ii., 54).—Fe, Cr, Al are completely separated from Mn, Zn, Ni, Co by boiling with excess of  $\text{NaNO}_2$ . It is better to have Fe in the ferrous state.
322. **Ether**.—SKEY (*C. N.*, xvi., 201) suggests a separation by abstracting the Fe with ether from a solution of the sulpho-cyanides.

323. *Nitroso-β-naphthol*.—KNORRE (*C. N.*, lix., 232 ; *J. I. S. I.*, 1887, i., 470).—Fe must be present as sulphate or chloride ; neutralized solution precipitated with at least ten times as much of the reagent, dissolved in acetic acid, as there is Fe present. By the same process Fe is separated from Cr, Ni, Zn, and Al. (See also DE KONINCK, *Chem. News*, lxii., 19.)
324. BURGASS (*J. C. S.*, lxxii., ii., 162).—Nitroso-β-naphthol precipitates Cu, Co, and Fe completely ; Mn, Hg, Ni, Cr, Pb, Zn, Al, Cd, Mg, Ca, Bi, Sb, and As remain in solution.
325. *Electrolytic*.—KOEPEL (*J. C. S.*, lxxiv., ii., 354).—Solution of Fe and Mn sulphates are poured into boiling sodium pyrophosphate. The Fe is deposited from the clear solution.

*b. Precipitating the Manganese :*

326. BEILSTEIN and JAWAIN (*C. N.*, xl., 300 ; *J. I. S. I.*, 1880, 354).—Solution of the metals poured into concentrated KCN ; the Mn is precipitated with iodine and converted into sulphide. Describes also the chlorate process, which is really a separation in which the manganese is precipitated.
327. MOORE (*C. N.*, lvii., 125).—Sodium carbonate in excess added to concentrated solution of the metals ; dissolve precipitate in KCN, add a little KHO, and precipitate Mn with  $H_2O_2$ . The Mn may also be precipitated with  $H_2S$ . Ni and Co are also precipitated.
328. CLASSEN (*C. N.*, xl., 33).—Manganous solutions are precipitated by neutral potassium oxalate ; the precipitate being soluble in excess. The potassium manganous oxalate is decomposed by concentrated acetic acid, but the potassium ferric oxalate remains dissolved. Zn or Mg chlorides, used to obviate influence of alkaline chlorides. The process separates Ca, Co, Ni, and Cu from Fe and Al, and is later elaborated (*C. N.*, xl., 196) to cover a number of other separations. (See 527.)
329. BLUM (*C. N.*, lv., 236).—HCl solution of chlorides mixed with tartaric acid, so that no precipitate is formed with ammonia ; ferri-cyanide added. Mn, Ni, Co, and Zn are precipitated. Filters badly.
330. ENGELS (*J. C. S.*, lxxiv., ii., 192).— $MnO_2$  is precipitated by the electric current from an acidulated solution of the sulphates.

## II. Separating other Elements from Manganese.

331. *Aluminium*.—ROSE (*C. N.*, ii., 266).—Add  $(NH_4)Cl$ , boil, add ammonia, and boil off excess. Precipitate perfectly free from Mn.
332. *Nickel and Cobalt*.—TERRIEL (*C. N.*, xiii., 133).—Permanganate completely precipitates manganese from ammoniacal solutions.
333. JANNASCH and FRANZEK (*J. I. S. I.*, 1892, i., 493).—Solution of the

- sulphates converted to double cyanides and Mn precipitated with  $\text{H}_2\text{O}_2$ . Re-precipitation recommended (*J. C. S.*, lxx., ii., 548).
334. *Nickel, Cobalt, and Zinc*.—GIBBS (*C. N.*, xi., 148).—Precipitates in acetic solutions with  $\text{H}_2\text{S}$ .
335. CLARK (*J. C. S.*, lxiii., 1082).—Sodium peroxide precipitates Mn from ammoniacal solutions free from Zn. Re-precipitation is required in order to separate Ni and Co.
- 335a. TAMM (*C. N.*, xxvi., 37).—Mn is precipitated with  $(\text{NH}_4)_2\text{CO}_3$  free from Ni and Zn.
336. *Zinc*.—JANNASCH and NIEDERHOFHEIM (*C. N.*, lxxv., 159).—A mixture of KCN and KHO are added until precipitate is re-dissolved. Mn precipitated with  $\text{H}_2\text{O}_2$ .
337. RENARD (*C. N.*, xx., 35).—Mn precipitated with sodium phosphate and ammonia.
338. BAYLEY (*J. S. C. I.*, 1887, 499).—Zn precipitated with  $\text{H}_2\text{S}$  from a solution containing free phosphoric acid.
339. NEUMANN (*J. S. C. I.*, 1889, 62).—Zn may be precipitated as sulphide from formic acid solutions free from Mn, Ni, or Fe.
- Separations with  $\text{H}_2\text{O}_2$* .—Mn is separated from a number of elements by adding the mixture to an alkaline solution of  $\text{H}_2\text{O}_2$ ; the procedure is very similar in each case. The references are :
340. *Mercury*.—JANNASCH (*C. N.*, lxxii., 65 ; and *J. C. S.*, lxviii., ii., 332).
341. *Silver*.—JANNASCH and KAMMERER (*C. N.*, lxxii., 91 ; and *J. C. S.*, lxviii., ii., 423).
342. *Arsenic*.—JANNASCH and KAMMERER (*J. C. S.*, lxx., ii., 221).
343. *Chromium*.—JANNASCH and CLOEDT (*J. C. S.*, lxx., ii., 222).
344. *Zinc*.—JANNASCH and CLOEDT (*J. C. S.*, lxx., ii., 220 and 546). Also JANNASCH and MACGREGORY (*J. C. S.*, lx., 963).
345. *Copper*.—JANNASCH (*J. C. S.*, lxx., ii., 546).
346. *Copper and Cadmium*.—JANNASCH and ROTTGEN (*J. C. S.*, lxviii., ii., 331).
347. *Tungsten*.—TAGGART and SMITH (*C. N.*, lxxv., 26).—Neither digestion with ammonium sulphide and  $(\text{NH}_4)\text{Cl}$  nor with  $\text{K}_2\text{CO}_3$  effects a complete separation.
348. *Phosphorus*.—GRANGER (*C. N.*, lxxv., 95).—Fuse with KHO, evaporate acid solution to dryness, re-dissolve, and precipitate with ammonium sulphide.
349. *Chromic Acid*.—BREARLEY (*C. N.*, lxxvii., 131).—Add sodium carbonate to cold solution, and filter at once or after heating to boiling-point. Precipitation with soluble phosphate, using considerable excess, in ammoniacal solution.
350. *Copper*.—KNORRE (*J. C. S.*, lii., 530).—To acid solution of sulphates or chlorides add nitroso- $\beta$ -naphthol in acetic acid. Cu is precipitated.
351. FERNBERGER and SMITH (*J. S. C. I.*, 1900, 53).—Electro-separation of Cu.



## III. Gravimetric Estimation of Manganese.

## a. As Mangano-manganic Oxide :

352. EGGERTZ (*C. N.*, xviii., 232).—Precipitate with Br, wash with cold 1 per cent HCl, dry at 100° C., and weigh as hydrated oxide (59.21 per cent. Mn), or ignite to  $Mn_3O_4$ .
353. KESSLER (*C. N.*, xxvii., 14).—Precipitates with Br and sodium acetate.
354. ABEL (*C. N.*, vi., 125).—Precipitates Mn from ammoniacal solution with bromine.
355. PIESSE (*C. N.*, xxix., 110).—Precipitates with Br and ammonia, and allows to stand eighteen hours.
356. WILLIS (*C. N.*, xxix., 150).—Uses more Br and ammonia, and points out that the precipitation of the Mn is immediately complete.
357. RIGGS (*J. C. S.*, lxii., 536).—Bromine should be added to the hot ammoniacal filtrate.
358. HOLTHOF (*J. S. C. I.*, 1885, 367).—Precipitate  $Mn(HO)_2$  with Br and large excess  $(NH_4)HO$ . Alkalis, alkaline earths, Cu, Zn, and Mg are partly carried down. A re-precipitation in presence of much  $AmCl$  with  $Am_2CO_3$ .
359. MULLER (*J. I. S. I.*, 1886, 392).—Acetate separation of Fe. Precipitates Mn with  $H_2O_2$  and  $(NH_4)HO$ , and ignites.
360. MEINECKE (*J. I. S. I.*, 1887, i., 469).—ZnO separation of Fe; filtrate mixed with  $HgO$ ; heat to boiling-point and precipitate with Br. The precipitate is washed with dilute  $HNO_3$  (free from nitrous) and ignited.
361. JUPTNER (*J. I. S. I.*, 1885, 247).—Precipitated sulphide dissolved in acetic acid, evaporated, and ignited to  $Mn_3O_4$ .
362. KERN (*C. N.*, xxxii., 100).—Fe and Mn precipitated with KHO, heated in H; mixture powdered under naphtha oil; Fe separated with magnet, and MnO ignited to  $Mn_3O_4$ .
363. PARKER (*C. N.*, xxii., 186).—Spiegels contain Cu up to 0.5 per cent.; this is precipitated by the Br and ammonia, and to some extent if Mn is precipitated as phosphate.
364. MATHESIUS (*C. N.*, liii., 74).—Oxides of Mn ignited along with  $NH_4Cl$  are partly volatilized. (See 313a.)
365. PICKERING (*C. N.*, xliii., 189).—The degree of oxidation of  $MnO_2$ .  $MnO$  compounds is influenced by heating in air at 100° C., or even by boiling in water. Compounds variously oxygenated are produced when oxides of manganese are heated to redness in a platinum dish over a Bunsen. Permeability of the platinum probable cause of the error.
366. PATTINSON (*J. S. C. I.*, 1891, 333).— $Mn_3O_4$  formed only by ignition at almost white heat, the oxide being protected from reducing agents; heat of a Bunsen not sufficient to form  $Mn_3O_4$ ; heating over gas

blowpipe dangerous, owing to reducing gases permeating the crucible. All ignitions in air need confirmation by a determination of the available oxygen. Modified form and interference of Ni, Co, Cu, Pb, and Cr with 501.

367. GORGEU (*J. C. S.*, liv., 653).—After heating to bright redness,  $\text{Mn}_3\text{O}_4$  absorbs absolutely no oxygen on cooling.
368. MEINECKE (*J. C. S.*, lvi., 311).—To prevent the ignited precipitate containing fixed alkali, it should be heated with  $(\text{NH}_4)\text{Cl}$  and ammonia before filtering.
369. GOOCH and AUSTIN (*C. N.*, lxxvii., 255).—Ignition to  $\text{Mn}_3\text{O}_4$  may be made in strong Bunsen or blast-lamp in such a way that an oxidizing flame covers the entire wall of the crucible.

*b. Estimation of Mn as Pyrophosphate. (See also 471.)*

370. GIBBS (*C. N.*, xvii., 195).—Describes the precipitation as ammonium-manganese phosphate. Refers to other metals precipitable as ammonio-phosphates.
371. GOOCH and AUSTIN (*C. N.*, lxxviii., 239).—The success of the precipitation depends mainly on the change of  $\text{Mn}_3\text{P}_2\text{O}_8$  to  $\text{NH}_4\text{MnPO}_4$ ; the presence of  $(\text{NH}_4)\text{Cl}$  or a substitute essential to completeness of this change; the proportion  $(\text{NH}_4)\text{Cl}$  to final  $\text{Mn}_2\text{P}_2\text{O}_7$  should be at least 50 to 1; large excess not harmful; ammonia used in slight excess; glass vessels available if operation is rapid.
372. MCKENNA (*C. N.*, lxiii., 184).—Compares Gibb's original process (370) and Blair's (*Chem. Anal. of Iron*) modification. The precipitate must be quite crystalline; a trace of Mn always found in the filtrate; hot water,  $(\text{NH}_4)\text{HO}$ , and  $(\text{NH}_4)\text{NO}_3$  all slightly dissolve the precipitate; glass vessels may be used.
373. NORRIS (*J. S. C. I.*, 1901, 551).—Ether-acetone separation of Mn and Fe and estimation of former as phosphate. Some minor impurities of Mn alloys and ores are simultaneously prepared for estimation.
374. BOYD (*J. S. C. I.*, 1890, 973).—Phosphate may be precipitated in and filtered from hot solutions without detriment. Similar process for zinc.
375. BOTTGER (*C. N.*, lxxxii., 247).—Modified phosphate precipitation; explanations from ionic point of view.
376. DAKIN (*C. N.*, lxxxiii., 37).—Experimental inquiry; weighs either as pyrophosphate or double ammonium salt.

*c. Estimation of Mn as Sulphate:*

377. GOOCH and AUSTIN (*C. N.*, lxxvii., 256).—Estimation as sulphate formerly recognized procedure; definite condition of hydration thought hard to attain to. Volhard used a ring burner in iron casing, and obtained excellent results; authors support crucible on a

triangle within a larger crucible, and are able to heat the outer one to redness without risk ; good results ; regarded as most reliable of the gravimetric processes.

378. REINHARDT (*J. S. C. I.*, 1886, 391).—Methods for analysis of mangani-ferous ores. Mn weighed as sulphate.

*d. Estimation of Mn as Sulphide.* (See also 540.)

379. ROSE (*C. N.*, ii., 302).—Precipitated sulphide not wholly insoluble, especially in liquids containing ammonium salts ; the precipitate is deposited slowly.
380. BLUM (*J. I. S. I.*, 1890, i., 372).—In the presence of Ca the precipitation should be made in boiling solutions and rapidly filtered, as calcium hyposulphite may crystallize out.
381. FRESSENIUS (*C. N.*, iv., 150).—Ammonium sulphide does not precipitate very dilute solutions of Mn ;  $(\text{NH}_4)\text{Cl}$  favours the precipitation after some time.
382. MEINECKE (*J. S. C. I.*, 1888, 236).—Precipitated from boiling solutions containing excess of ammonia ; a trace remains unprecipitated ; large amounts of  $(\text{NH}_4)\text{Cl}$ ,  $\text{NaCl}$ , or  $\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)$  are without influence. Satisfactorily separates Ca and Mg.
383. MURMANN (*J. S. C. I.*, 1898, 1186).—Mn precipitated as sulphide in the presence of  $\text{HgCl}_2$  quickly deposits, and may be washed without passing the filter. Hg is removed by subsequent ignition.
384. PATTINSON (*C. N.*, lxxxi., 193).—The filtrate from the sulphide always contains a little Mn, and the precipitate in case of ores may contain Ba, Co, Ca, or Mg.

*e. Precipitation of Mn as Carbonate :*

385. FORBES (*C. N.*, xvi., 105).—Precipitates with sodium carbonate.
386. TOSH (*C. N.*, xvi., 168).—Re-dissolves precipitated sulphide in  $\text{HCl}$ , precipitates with sodium carbonate, and ignites to  $\text{Mn}_3\text{O}_4$ .
387. TAMM (GUYARD) (*C. N.*, xxvi., 37).—Precipitates with ammonium carbonate ; claims this, amid much rattle, as a startling discovery. Allen (*C. N.*, xxvi., 81) speaks of it as an old process.
388. AUSTIN (*C. N.*, lxxvii., 242).—Precipitation as carbonate complete ; presence of  $(\text{NH}_4)\text{Cl}$  necessary to ensure filterable precipitate. Preferable to weigh as sulphate.
389. GORGEU (*C. N.*, lix., 277).—At the common temperature carbonate or oxide of Mn cannot absorb from air or aerated water a proportion of O greater than corresponds to  $\text{MnO}_2$ .  $\text{MnO}$ . (See 506.)

*f. Estimation of Manganese Electrolytically :*

390. RICHE (*C. N.*, xxxvi., 90).—Deposited as peroxide. Cu, Ni, Co, Zn, Mg, Al, alkalis or alkaline earths, may be present. Large amounts of Fe injurious.

391. KÆPPEL (*C. N.*, lxxvii., 201 ; and lxxix., 195).—Deposited partly as metal and partly as  $\text{MnO}_2$  from neutral or faintly acid solutions ; very strong current used ; addition of acetone improves results.
392. VORTMANN (*J. I. S. I.*, 1892, i., 490).—Mn and Hg precipitated simultaneously as an amalgam ; Zn, Pb, Cd, Sb, As, and Bi, which do not form coherent deposits, can be similarly estimated. (See *C. N.*, lxiv., 227, etc.)
393. ENGELS (*J. C. S.*, lxxiv., ii., 52).—Deposited at  $80^\circ \text{C}$ . from solutions containing Cr alum, or alcohol and ammonium acetate.
394. BRAND (*J. C. S.*, lviii., 294).—After dissolving in pyrophosphate,  $\text{MnO}_2$  is deposited, adhering firmly. Ignited to  $\text{Mn}_3\text{O}_4$ .
395. RUDORFF (*J. C. S.*, lxiv., ii., 94).—Mn should be present as sulphate ; deposited hydrated peroxide dried at  $60^\circ$  and weighed.
396. CLASSEN (*J. C. S.*, lxvi., ii., 480).—Solution electrolyzed in presence of acetic acid ; peroxide ignited to  $\text{Mn}_3\text{O}_4$ .
397. HJØRNS (*C. N.*, lxxx., 15).—Deposited from  $\text{HNO}_3$  solutions ; precipitated  $\text{MnO}_2$  ignited to  $\text{Mn}_3\text{O}_4$ .
398. VOLMAN (*J. C. S.*, lxxiv., ii., 50).—Deposited from  $\text{HNO}_3$  solution at  $50^\circ$  ; small current ; solution in oxalate, acetic acid, or pyrophosphate do not give good results.
399. GRÖGER (*J. C. S.*, lxviii., ii., 419).—Electro-deposited Mn not entirely peroxide. Only 94 to 96 per cent. estimated by KI and thiosulphate, on the assumption that the precipitate is  $\text{MnO}_2$ .

*g. Estimation of Mn (Miscellaneous):*

400. CARNOT (*C. N.*, lvi., 16).—Precipitated as vanadate from an ammonical solution. Ignited precipitate has the composition  $2\text{MnO} \cdot \text{V}_2\text{O}_5$ .

#### IV. Volumetric Estimation of Manganese.

*a. Titrations with Standard Permanganate :*

401. GUYARD (*C. N.*, viii., 292).—Titration at  $80^\circ \text{C}$ . Associated metals are converted to peroxides, and do not interfere. The process separates Mn from alkalis, Ca, Sr, Mg, Ni, Co, Zn, and Ur. (Some of the separations are not nearly exact ones.—H. B.) Discusses three permanganates of MnO :— $5\text{MnO} \cdot \text{Mn}_2\text{O}_7$ ,  $4\text{MnO} \cdot \text{Mn}_2\text{O}_7$ , and  $3\text{MnO} \cdot \text{Mn}_2\text{O}_7$ .
402. HABICH (*C. N.*, xii., 58).—Dilute  $\text{H}_2\text{SO}_4$  and HCl ; lower oxides of Ni and Co, ZnO,  $\text{Al}_2\text{O}_3$ , and CaO do not interfere with Guyard's process. Strong HCl or  $\text{H}_2\text{SO}_4$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Cr}_2\text{O}_3$  render the process useless.
403. GORGEU (*J. I. S. I.*, 1894, i., 613).—Results by Guyard's process too low, partly on account of the acidity of the liquid. Donath's modification (see 416) also gives inexact results unless the solutions are slowly mixed. Criticises Guyard's views (see 401) concerning existence and constitution of the compounds formed during the titration.

404. VOLHARD (*C. N.*, xl., 207).—Manganous solution mixed with  $\text{ZnSO}_4$ , made faintly acid with  $\text{HNO}_3$ , and titrated near boiling-point to a permanent red colour.
405. AUCHY (*C. N.*, lxxiv., 214).—Examination of Volhard's process for estimation of Mn in steels. Add ZnO to cold solution until Fe is precipitated, then excess of ZnO; titrate at boiling-point, and deduct 0.02 per cent.
406. HASWELL (*J. I. S. I.*, 1882, 743).—Acidification with a few drops of  $\text{HNO}_3$  previous to titration counteracts traces of organic matter. Standardize permanganate with KI and thiosulphate.
407. DAW (*C. N.*, lxxix., 25).—Titrations with permanganate are subject to error on account of organic matter, reckless addition of ZnO, and standardizing solutions with Fe instead of Mn. Process described to eliminate these errors. BREARLEY (*C. N.*, lxxix., 47) takes exception to permanganate being standardized by the  $\text{Mn}_3\text{O}_4$  finally heated over a blast-lamp. The validity of this procedure is discussed (pages 58, 83, and 104).
408. WOLFF (*J. I. S. I.*, 1885, 301).—Separates Fe with ZnO; no filtration; excess ZnO to be avoided;  $\text{KClO}_3$  used to oxidize Fe;  $\text{HNO}_3$  leads to organic compounds, which interfere with titration. Results slightly low.
409. REIS (*J. S. C. I.*, 1893, 378).—Modification of Wolff's process. See also BOERNER (*J. I. S. I.*, 1901, ii., 519).
410. MEINECKE (*J. S. C. I.*, 1886, 508).—To nitro-sulphuric acid solution of Fe add  $\text{CrO}_3 + \text{BaCl}_2 + \text{ZnO}$ ; pour filtrate into excess permanganate, and titrate back with  $\text{SbCl}_3$ . (See 494.)
411. SARNSTROM (*C. N.*, xlvii., 177).—Sodium bicarbonate added in small quantities until Fe is precipitated; titration by Guyard's process without filtering off the Fe.
412. AUCHY (*J. C. S.*, lxxii., ii., 603).—The danger of Mn being carried down by the precipitated ferric oxide greatly lessened if about 7 grms.  $(\text{NH}_4)\text{Cl}$  is added before the sodium carbonate in Sarnstrom's process.
413. MIXER and DUBOIS (*C. N.*, lxxv., 51).—A study of Sarnstrom's method. Add  $\text{Fe}_2\text{Cl}_6$  if Fe is low; use large amounts  $\text{HCl}$ , so as to generate  $\text{CO}_2$ ; large excess carbonate to be avoided. Not reliable for high percentages.
414. BREARLEY (*C. N.*, lxxv., 13).—Acetate separation of Fe; faintly acid filtrate poured into excess of permanganate mixed with  $\text{ZnSO}_4$  (Wright and Meinecke's modification of Guyard's process, see *J. C. S. Trans.*, 1880), and excess permanganate titrated; or the precipitated  $\text{MnO}_2$  may be estimated. Excessive ammonium salts to be avoided (see 425). Describes syphon filter and general corrections for hot aliquot filtrations.
415. SCHÖFFEL and DONATH (*J. C. S.*, lii., 399).—Neutralize with sodium carbonate; add to permanganate and  $\text{ZnSO}_4$  and titrate excess with arsenious acid.

416. DONATH (*C. N.*, xliii., 253 ; and SCHÖFFEL and DONATH, *J. I. S. I.*, 1883, 381).—Neutral solution of Mn salt flows into hot alkaline permanganate ; process ended when supernatant liquid is colourless ; Fe present as per-salt does not interfere. Similar process for estimating Cr in presence of Fe and Al.
417. SCHÖFFEL and DONATH (*J. I. S. I.*, 1887, i., 469).—Fe separated with ZnO ; without filtration, run into boiling  $\text{KMnO}_4 + \text{ZnSO}_4$ —this to avoid formation of lower oxides than  $\text{MnO}_2$ . Excess permanganate determined with arsenious acid.
418. GIORGIS (*J. I. S. I.*, 1897, ii., 498 ; and *J. C. S.*, lxxii., ii., 350).—Neutralized solution of Fe and Mn boiled with permanganate and large amount of sodium nitrate ; excess permanganate determined. Similar process for Cr if Mn is absent or present in known amount.
419. GHILIAN (*C. N.*, lix., 121).—Titration in presence of ZnO without filtering off Fe. Twenty-five assays in half an hour.
420. BRAND (*J. I. S. I.*, 1887, ii., 368 ; and 1888, i., 375 ; REIS, *J. C. S.*, lxiv., ii., 304).—Sample dissolved in nitro-sulphuric acid, oxidized with  $\text{HNO}_3$  and barium peroxide,  $\text{H}_2\text{O}_2$  boiled off, Fe precipitated with ZnO, and solution titrated ; precipitate settles rapidly ; continuous working with two burettes.
421. RUBRICIUS (*J. I. S. I.*, 1892, ii., 512).—Precipitates Fe with ZnO, and adds  $\text{MgSO}_4$  previous to titration.
422. JOLLES (*J. S. C. I.*, 1889, 819).—MnO solution added to faintly alkaline solution of standard manganate until it is decolourized ; the precipitate is  $\text{MnO}_2$ . Co estimated similarly.

*Standard Solutions and General Notes :*

423. DUNN (*C. N.*, xlv., 137).—Mixed solutions of  $\text{MnSO}_4$  and  $\text{KMnO}_4$  evolve little or no gas in the cold ; on heating, O is evolved if the permanganate is in excess.
424. MORSE and REESE (*C. N.*, lxxviii., 77).—Permanganate is reduced and O evolved if  $\text{MnO}_2$  is present. To this cause is ascribed the instability of  $\text{KMnO}_4$  solutions ; they should always be carefully filtered.
425. TAMM (*C. N.*, xxv., 26).—Permanganate as an oxidizing agent can convert ammonia into  $\text{HNO}_3$ .
426. MEYER and RECKLINGHAUSEN (*J. C. S.*, lxxii., ii., 19).—H and CO are slowly oxidized by a solution of  $\text{KMnO}_4$ .
427. HARCOURT (*C. N.*, xiii., 293).—Speed of the reaction between permanganate and oxalic acid depends on the relation between permanganate, oxalic acid, manganous sulphate, and sulphuric acid.
428. DYMOND and HUGHES (*J. C. S.*, lxxi., 314).—On titrating  $\text{H}_2\text{SO}_3$  with  $\text{KMnO}_4$ , only 89 per cent of that required to form  $\text{H}_2\text{SO}_4$  is used ; due to formation of dithionic acid. Same amount formed under varying conditions.
429. LONGI and CAMILLA (*J. C. S.*, lxxii., ii., 387).— $\text{MnO}_2$  adhering to vessel during precipitation due to dirt, and may be prevented by washing

with  $\text{H}_2\text{SO}_4 + \text{CrO}_3$ . Ni,  $\text{CrO}_3$ , Co, Pb do not interfere with permanganate titration of MnO.

430. LUNGE (*J. S. C. I.*, 1890, 21).—Permanganate standardized in acid solution with  $\text{H}_2\text{O}_2$ ; evolved O measured. A similar process serves to determine available oxygen in pyrolusite, Weldon mud, etc.
431. MORSE and CHAMBERS (*J. C. S.*, lxx., ii., 388).—In presence of a neutral reducing agent, such as  $\text{H}_2\text{O}_2$ , permanganate may be standardized with  $\text{H}_2\text{SO}_4$ , or conversely.
432. RIEGLER (*J. C. S.*, lxx., ii., 676).—Solution of oxalic acid containing large amount of  $\text{H}_2\text{SO}_4$  keeps unchanged for a year.
433. LENZ (*J. C. S.*, xlviii., 598).—Ten grms. boric acid per litre prevents the decomposition of oxalic acid.
434. HAMPE (*C. N.*, xlvii., 260).—Pure dehydrated oxalic acid is obtained by sublimation, and kept over  $\text{H}_2\text{SO}_4$ .
435. M'DIRBY (*C. N.*, xxx., 142).—Permanganate standardized by simply dissolving piano-wire is inaccurate. The small amount of C existing in the Fe is oxidized also, and errors of 1 to 2 per cent. are caused. Berthelot has previously drawn attention to this point. See also WDOWISZEWSKI (*J. I. S. I.*, 1901, ii., 521) and 406.

*b. Oxidations to Permanganate:*

436. GIBBS (*C. N.*, xi., 147).—Has recommended boiling with  $\text{PbO}_2$  to separate Mn from alkaline earths. A compound,  $\text{MnO}_2 + 4\text{PbO}_2$ , is formed. [This appears to be the source of error, more or less evident, whenever more than about 0.01 gm. of Mn is boiled in an acid solution with  $\text{PbO}_2$ .—H. B.]
437. MORSE (*J. C. S.*, lxxii., ii., 145).—In presence of  $\text{HNO}_3$  the following reaction occurs:— $2\text{HMnO}_4 + 3\text{PbO}_2 = \text{H}_2\text{O} + 2\text{MnO}_2 + 3\text{PbO} + 3\text{O}_2$ .
438. LECLERC (*C. N.*, xxvi., 297) and PICHARD (*C. N.*, lxxvii., 108).—Oxidizes an acid solution of soils, etc., with red lead; it is necessary to destroy organic matter. Not possible to titrate with  $\text{FeSO}_4$  on account of  $\text{PbSO}_4$  (see 450), or oxalic acid on account of  $\text{PbCO}_3$  (see 448). Titrates with  $\text{HgNO}_3$ , liquid to be freely acid so as to prevent precipitation of Mn oxides (Guyard's reaction).
439. PECHARD (*C. N.*, xxvii., 85).—Effects solution by fusing with sodium carbonate. Compares with standard permanganate to 1/10,000 by diluting largely.
440. DESHAY (*C. N.*, xxxviii., 70).—Nitric or nitro-sulphuric acid solution of the sample; oxidizes with  $\text{PbO}_2$ . Always the colouration is stronger as the amount of Mn increases. Tone varies according to origin and degree of oxidation. Essential to operate under like conditions. Titrates with sodium arsenite.
441. JERVIS (*C. N.*, lxxxi., 171).—By oxidizing increasing amounts of Mn with  $\text{Pb}_3\text{O}_4$  a point is reached when the more Mn present the less shows as  $\text{KMnO}_4$ . Titrate with  $\text{FeSO}_4$ ; but in presence of  $\text{CrO}_3$  with oxalic acid.



442. PETERS (*C. N.*, xxxiii., 35). — Dissolve in  $\text{HNO}_3$ ; oxidizes with  $\text{PbO}_2$ . Finds 1 per cent. to be the limit, using 0.1 grm. of the sample. For spiegels, works on 0.004 grm. Combined carbon does not interfere. Also LEDEBUR (*J. S. C. I.*, 1883, 249).
443. CHATARD (*C. N.*, xxiv., 196).—Used for dolomite and limestones. Fails for large amounts of Mn. Longer the mixture is boiled more permanganate is there formed, but no limit attainable.
444. MORGAN (*C. N.*, lvi., 82).—Oxidation with  $\text{PbO}_2$ . Colour comparison. Estimates Mn in the sample which has served for colorimetric estimation of carbon.
445. SCHLAGDENHAUFFEN (*J. C. S.*, xlvi., 442). — Oxidation with  $\text{PbO}_2$ . Concentration of solution not less than 0.1 per cent. Mn or 2 per cent.  $\text{HNO}_3$ . Titrate in very acid solution.
446. HUNT (*J. I. S. I.*, 1886, 1020).— $\text{HNO}_3$  used should be free from Cl or nitrous fumes, and throughout the process should be 1.20 sp. gr.; heats in  $\text{CaCl}_2$  bath; compares colours. CHEEVER (*ibid.*) considers the method unreliable.
447. IBBOTSON and BREARLEY (*C. N.*, lxxxii., 209).—Tungsten metal or alloys after opening out with  $\text{HF} + \text{HNO}_3$  are boiled with  $\text{Pb}_3\text{O}_4$  and  $\text{KMnO}_4$  titrated with  $\text{FeSO}_4$ .
448. THORPE and HAMBLY (*J. C. S.*, liii., 182).—Oxidation with  $\text{PbO}_2$  in nitro-sulphuric solution, and titration with ammonium oxalate. Not more than 0.01 grm. Mn should be present.
449. BABBIT (*J. I. S. I.*, 1887, ii., 369).—Oxidation with  $\text{PbO}_2$ : supernatant liquid decanted through asbestos, and residue boiled with 20 per cent.  $\text{HNO}_3$  so long as the decanted liquid is coloured.
450. WEISMANN (*J. I. S. I.*, 1888, i., 377).—Solution in nitro-sulphuric acid oxidized with  $\text{PbO}_2$ , and titrated with  $\text{FeSO}_4$ .
451. SCHNEIDER (*J. I. S. I.*, 1892, ii., 512).—As Weismann; titrates with  $\text{FeSO}_4$  and  $\text{KMnO}_4$ , Cr and Mn may be thus estimated together. Two grms. of sample used.
452. SCHNEIDER (*J. C. S.*, lxxiv., ii., 94) — Titration of the permanganate solution with  $\text{H}_2\text{O}_2$ .
453. VAN GRUNDY (*J. I. S. I.*, 1892, ii., 512).—Oxidation with  $\text{PbO}_2$ , and titration with arsenious acid. Method spoken of as Textors.
454. KONINCK (*C. N.*, lix., 230).—Commercial  $\text{PbO}_2$  prepared by treating alkaline lead solutions with Cl; this gas carries  $\text{MnCl}_2$  derived from its preparation. Hence the presence of Mn in  $\text{PbO}_2$ . (Mn-free red lead easy to obtain.—H. B.)
455. MARSHALL (*C. N.*, lxxxiii., 76).—Permanganate is formed on warming MnO solutions with persulphate in presence of  $\text{AgNO}_3$ ; shows with 0.001 milligrams Mn in 1 c.c.
456. WALTERS (*C. N.*, lxxxiv., 239).—Has adapted the above to the estimation of the Mn in steels, etc.
457. SCHNEIDER (*J. S. C. I.*, 1888, 525 and 693).—Bismuth tetroxide in  $\text{HNO}_3$  solution converts Mn to permanganate. Titrate with  $\text{H}_2\text{O}_2$  or



oxalic acid ; adapts to assay of metals, ores, slags, and gives mode of preparing tetroxide. MIGNOT (*J. S. C. I.*, 1900, 856) says it is not applicable if over 1 per cent. Cr is present.

458. REDDROP and RAMAGE (*J. C. S.*, lxxvii., 268).—A modification of 457. Permanganate filtered into excess  $\text{H}_2\text{O}_2$  in  $\text{HNO}_3$ , and titrated back with  $\text{KMnO}_4$ . Cu and Ni are without effect. Cr and Co = 5 per cent. cause only slightly high results. Available for any amount of Mn, and completed in fifteen minutes.

459. RAMAGE (*C. N.*, lxxxiv., 209).—Modifications of 458.

460. IBBOTSON and BREARLEY (*ibid.*, p. 247, 269, etc.) further modifications of 458 and behaviour in presence of Cr, W, Mo, V, Ti, etc.

461. DUFFY (*C. N.*, lxxxiv., 248).—Uses 458 as a colorimetric process.

462. J. T. (*C. N.*, lxxxiii., 25).—Fuse ferro-chromium with  $\text{Na}_2\text{O}_2$ , filter, dissolve residue in  $\text{HNO}_3 + \text{SO}_2$  and apply 458.

463. OSMOND (*J. I. S. I.*, 1885, 275).—Dissolve in  $\text{HCl}$ , evaporate : dissolve in  $\text{HNO}_3$ , add sodium metaphosphate and  $\text{PbO}_2$ . Filtrate compared with standard. The error is 1/50th.  $\text{PbO}_2$  may be replaced by current of ozonized oxygen.

464. ROSSI (*J. I. S. I.*, 1891, i., 438 ; and 1892, i., 491).—Like Osmond, but  $\text{CaCO}_3$  instead of  $\text{PbO}_2$ . When Cl is evolved the solution is filtered and compared with standard.

465. MOORE (*C. N.*, lxiii., 66).—The Mn is oxidized to manganic metaphosphate by means of phosphoric acid and chlorate. The violet liquid is titrated with  $\text{FeSO}_4$  and  $\text{KMnO}_4$ . Cr is the only metal that interferes.<sup>1</sup>

### c. Oxidation to Higher Oxides of Mn.

#### c. 1. The Chlorate Process. (See also 326.)

466. HANNAY (*C. N.*, xxxvi., 212).— $\text{MnO}_2$  precipitated by heating with  $\text{HNO}_3$  and  $\text{KClO}_3$ . In presence of Fe a double manganate of Fe and Mn is precipitated. Refers to the process as a means of separating Fe and Al.

467. STORER (*C. N.*, xxi., 195).—Oxidizing value of  $\text{HNO}_3$  and  $\text{KClO}_3$  applied to assays of S and Cr compounds, etc.

468. WILLIAMS (*J. I. S. I.*, 1881, 656).—Filter  $\text{MnO}_2$  from the strong acid solution. Titrate with oxalic acid and permanganate.

469. MEINECKE (*J. C. S.*, lii., 531).—In the presence of Fe, warm dilute  $\text{HNO}_3$  dissolves a little  $\text{MnO}_2$  as precipitated by the  $\text{KClO}_3$  process.

470. JULIAN (*C. N.*, lviii., 209 ; and *J. I. S. I.*, 1888, i., 376).—The precipitated solution is diluted, excess oxalic acid added, and titration with  $\text{KMnO}_4$  speedily made.  $\text{KMnO}_4$  standardized by adding oxalic acid to nitric solution from which  $\text{MnO}_2$  has been filtered. (*J. S. C. I.*, 1888, 185.) Uses  $\text{H}_2\text{O}_2$  instead of oxalic acid. (See also 1007.)

471. STONE (*J. I. S. I.*, 1883, 366).—The Mn precipitated with  $\text{KClO}_3$

<sup>1</sup>This and Nos. 463 and 464 are not oxidations to permanganate ; they are classed here, however, because the operations are very similar.

- approximates to  $10\text{MnO}_2 \cdot \text{MnO}$ , and therefore oxidimetric estimations give low results. The standard solutions should be standardized with a *spiegel* of known composition. . . . Separation with acetate and estimation as  $\text{Mn}_2\text{P}_2\text{O}_7$  most accurate gravimetric process.
472. RAYMOND, TROILIUS, and MACKINTOSH (*J. I. S. I.*, 1883, 783).— $\text{MnO}_2$  dissolved in  $\text{FeSO}_4$  and titrated. That the precipitate is not  $\text{MnO}_2$  strongly repudiated; necessary to divide  $\text{KClO}_3$  into small portions, and add alternately with strong  $\text{HNO}_3$  in order to secure  $\text{MnO}_2$ . (See also MACKINTOSH, *C. N.*, *xlvi*., 176.)
473. STONE (*C. N.*, *xlvi*., 273).—Defends his previous statement (see 471). The  $\text{MnO}_2$  may be filtered from the hot as well as from the cold solution.
474. MACKINTOSH (*C. N.*, *i*., 75).—Influence of organic matter and iron on the process. Results a trifle low. Low results may sometimes be due to  $\text{KCl}$  in the  $\text{KClO}_3$  giving rise to free  $\text{HCl}$ .
475. TROILIUS (*J. C. S.*, *xlvi*., 597).—The presence of  $\text{Fe}(\text{NO}_3)_3$  facilitates precipitation with  $\text{KClO}_3$ . Lead, Cu, Ni, and Co are precipitated with the  $\text{MnO}_2$ , and give high results.
476. RAYMOND (*C. N.*, *xlvi*., 23).—After precipitating  $\text{MnO}_2$ , the solution is diluted with hot water before filtering.
477. J. T. (*C. N.*, *lxxix*., 157).—Cr steels are incompletely soluble in  $\text{HNO}_3$ , hence the chlorate process is open to error by the unattacked metal being soluble in the acid solution of  $\text{FeSO}_4$  used in titrating.
478. HAMPE (*J. I. S. I.*, 1885, 652).—Gives equations representing the changes. Neither  $\text{HCl}$  nor  $\text{H}_2\text{SO}_4$  should be present, nor should large amounts of  $\text{H}_3\text{PO}_4$  (see 481). The  $\text{MnO}_2$  always contains foreign metals if such are in solution; Ni, Cu, Zn, and Sn are without influence; Co, Pb, and Bi cause high results; all such errors are eliminated by re-precipitating.  $\text{KClO}_3$  should be added, little by little, so long as green vapours are evolved, the solution boiled five or ten minutes, and filtered. Precipitate should be washed with water;  $\text{HNO}_3$  unnecessary and may contain nitrous acid.
479. CHEEVER (*J. I. S. I.*, 1885, 736).—Strong  $\text{HNO}_3$  is added finally, and the solution boiled to completely decompose  $\text{KClO}_3$ . Precipitate must be washed with nitrous-free  $\text{HNO}_3$ ; if washed with water Mn would be dissolved.
480. REIS (*J. C. S.*, *lxii*., 1132).—Modified process: use weaker acid and add  $\text{KClO}_3$  all at once. Hampe (*ibid.*) strongly protests against these modifications.
481. VIARD (*J. C. S.*, *lxii*., *ii*., 519).—Process inapplicable in the presence of phosphoric acid, owing to the formation of trimanganic phosphate. (See 465.)
482. GOOCH and AUSTIN (*C. N.*, *lxxvii*., 269).—Short historical account of the process, possibility of  $\text{KClO}_3$  being mechanically occluded in the  $\text{MnO}_2$ . Sodium chlorate more soluble and more easily decomposed; precipitation complete if solution is just raised to boiling after final

addition of  $\text{NaClO}_3$ ; prolonged boiling leads to loss, probably due to solvent action of lower oxides of N in absence of Cl, dilution before filtration tends to dissolve Mn; oxidimetric estimation with arsenious acid and iodine; the precipitate not  $\text{MnO}_2$ , error may be 2 per cent. or more if taken as such; solution of  $\text{MnO}_2$ , and precipitation at  $80^\circ\text{C}$ . with excess of permanganate in presence of  $\text{ZnSO}_4$ , throws down true  $\text{MnO}_2$ .

483. REINHARDT (*J. I. S. I.*, 1888, i., 377).— $\text{KClO}_3$  process not suitable for irons poor in Mn, and rich in Si. Describes a process similar to 494.
484. NORRIS (*C. N.*, lxiv., 242).—Process applied to slags by treating with  $\text{HNO}_3$  and adding HF, boiling off excess HF and adding  $\text{KClO}_3$ . For ores, solution is effected with  $\text{HNO}_3$ , tartaric acid, and HF.
485. FORD and BREGOWSKY (*J. C. S.*, lxxiv., ii., 540).— $\text{SiO}_2$  is decomposed with a few drops of HF. The Mn, especially in ores, is more completely precipitated when HF has been used. (See also BOLLING, *J. C. S.*, lxxx., ii., 626.)
486. JEAN (*J. C. S.*, lxiv., ii., 498).—Decomposes minerals with HCl, precipitates with sodium carbonate, dissolves in  $\text{HNO}_3$ , and precipitates Mn with  $\text{KClO}_3$ .

*c. 2. Other Oxidimetric Processes:*

487. PARRY (*C. N.*, xxix., 86).—Dissolve spiegel in  $\text{HNO}_3$ , evaporate, and heat to redness over Bunsen; cool, add sodium oxalate and HCl; heat, and collect  $\text{CO}_2$  in graduated tube.
488. GALBRAITH (*C. N.*, xxxiii., 47).—Proceeds like Parry, but adds  $\text{FeSO}_4$  and HCl and heats; the  $\text{FeSO}_4$  unoxidized by the Cl is titrated. (See 521.)
489. CARNOT (*C. N.*, lxviii., 51).—Evaporation of an  $\text{HNO}_3$  solution to dryness, and ignition of the residue, yields an oxide remote from  $\text{MnO}_2$ . Repeated ignition below  $200^\circ\text{C}$ . improves matters, but the practice is uncertain.
490. MEINECKE (*J. S. C. I.*, 1887, 457).—Precipitate Fe and Mn together with  $\text{HgO}$  and Br water. The  $\text{MnO}_2$  is determined with oxalic acid and  $\text{KMnO}_4$ .
491. REINHARDT (*C. N.*, lviii., 173).—Mn precipitated with sodium acetate, Br, and  $\text{ZnO}$ ; and  $\text{MnO}_2$  titrated with oxalic acid and  $\text{KMnO}_4$ .
492. LOW (*C. N.*, lxvii., 162).—Precipitation with  $\text{ZnO}$  and Br, and titration as above; ordinary constituents of ores do not interfere.
493. VORTMANN (*C. N.*, lxii., 251).—Alum, iodine solution, and  $\text{NaHO}$  are used to precipitate MnO solution. Iodine determined in filtrate with thiosulphate. Alum ensures formation of  $\text{MnO}_2$ . Process available in presence of Fe and Al.
494. REINHARDT (*J. I. S. I.*, 1886, 393).—Fe precipitated with acetate and partly removed; Mn precipitated with Br and ammonia;  $\text{MnO}_2$  titrated with  $\text{FeSO}_4$ , etc. This is spoken of as the Belani method.

- Describes Meinecke's titration (410). MÜLLER (*J. I. S. I.*, 1886, 1022) recommends Meinecke's process, especially for highly manganiferous alloys.
495. ROSENTHAL (*C. N.*, xxxvi., 147).—Precipitates as  $\text{MnO}_2 \cdot \text{H}_2\text{O}$  with  $\text{H}_2\text{O}_2$  and ammonia. Large excess of  $\text{H}_2\text{O}_2$  should be avoided; much  $(\text{NH}_4)\text{Cl}$  is objectionable.
496. BARLOW (*C. N.*, liii., 41).—Precipitates as above; precipitate completely insoluble in ammonium salts, and quite free from Ni, Co, or Zn. In presence of Fe the ignited  $\text{Fe}_2\text{O}_3 + \text{Mn}_3\text{O}_4$  is distilled with  $\text{HCl}$ , the Cl being absorbed in KI, etc. (See 526.)
497. CARNOT (*C. N.*, lix., 16).—Precipitates entirely as  $\text{MnO}_2$  with  $\text{H}_2\text{O}_2$  and ammonia. Estimated with oxalic acid and permanganate.
498. M'CULLOCH (*C. N.*, lix., 35).—Contends that Mn as precipitated by Carnot has varying composition, but approximately is  $\text{Mn}_7\text{O}_{13}$ . . . . CARNOT later (*C. N.*, lix., 48) says the Mn is precipitated as  $5\text{MnO}_2 \cdot \text{MnO}$ .
499. CARNOT (*J. I. S. I.*, 1893, ii., 531; 1895, i., 507).—Precipitate with  $\text{H}_2\text{O}_2$ , large amounts of  $\text{NH}_3$  salts give low results. Zn, Cu, Ni, and Co form complex salts ( $\text{ZnO} \cdot 5\text{MnO}_2$ ), but are eliminated by re-precipitating. Fe causes no inconvenience if below 60 per cent.; if more, preliminary separation with  $\text{KClO}_3$  (*C. N.*, lxviii., 51). Influence of  $\text{NH}_3$  salts overcome by large amounts of  $\text{H}_2\text{O}_2$ . Mn may also be precipitated with Br and  $(\text{NH}_4)\text{HO}$  in the cold as  $\text{Mn}_6\text{O}_{11}$ .
500. ULZER and BRUHL (*J. I. S. I.*, 1896, ii., 442).—Precipitate with  $\text{H}_2\text{O}_2$  and  $\text{NaHO}$ . Titrate with oxalic and  $\text{KMnO}_4$ .
501. PATTINSON (*C. N.*, xxxix., 201).—Precipitate by hypochlorite or bromine and  $\text{CaCO}_3$  in presence of  $\text{ZnCl}_2$  or  $\text{Fe}_2\text{Cl}_6$ , dissolve in  $\text{FeSO}_4$  and titrate excess with  $\text{K}_2\text{Cr}_2\text{O}_7$ . (See 539 and 366.)
502. LUNGE (*C. N.*, xli., 141).—That Ca salts have the same rôle as Zn salts in Pattinson's process. Processes for the analysis of Weldon mud discussed.
503. WELDON (*C. N.*, xli., 207).—Finds merely boiling slightly acidified  $\text{MnCl}_2$  with enough bleaching-powder to produce a faint  $\text{KMnO}_4$  colour to give results comparing with Pattinson's process, as 100 : 100.26.
504. ATKINSON (*J. S. C. I.*, 1886, 365, 422, and 467).—Pattinson's process gives slightly low results, due to incomplete oxidation of the Mn. Interference of foreign bodies with Br and  $\text{AmHO}$  precipitation; washes with dilute  $\text{AmHO}$ .
505. ROSSI (*J. I. S. I.*, 1891, i., 443).—Good account of Pattinson's process applied to manganiferous iron ores.
506. MITTENZWEY (*C. N.*, ix., 253).— $\text{MnO}$  solution made alkaline and shaken in a closed vessel. Amount of water needed to fill the partial vacuum equals amount of oxygen absorbed; calculation empirical; reaction certainly not so far as  $\text{MnO}_2$ . (See 389.) Other bodies similarly estimated.

507. SCHMID (*C. N.*, xiv., 107).—Freshly precipitated  $\text{MnO}_2$  precipitates  $\text{CuO}_2$  from  $\text{CuSO}_4$ .  $\text{CuO} = \text{MnO}_2$  quantitatively true.
508. CARNOT (*C. N.*, lxviii., 51).—Oxalic acid and  $\text{KMnO}_4$  are the best reagents for oxidimetric estimations.
509. KALMAN and SMOLKA (*C. N.*, li., 230 ; *J. I. S. I.*, 1885, 248).—Fuse with borax and alkaline carbonate, dissolve in  $\text{FeSO}_4$ , and titrate with permanganate. Suitable whenever the sample can be heated to  $\text{Mn}_3\text{O}_4$ .
510. MYHLERTZ (*J. C. S.*, lx., 366).—Fuse with sodium carbonate and  $\text{KNO}_3$ , digest with  $\text{H}_2\text{O}$ , reduce with alcohol ;  $\text{MnO}_2$  determined with  $\text{FeSO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ .
511. ALT (*J. C. S.*, lviii., 419).—By aspirating Br fumes through a previously boiled  $\text{MnO}$  solution containing  $(\text{NH}_4)\text{Cl}$  and  $\text{NH}_3$ ,  $\text{MnO}_2$  is precipitated without staining the sides of the flask.

*c 3. Available Oxygen in Ores, etc. :*

512. SHERER and RUMPF (*C. N.*, xx., 302 ; and xxi., 48).—Comparison of Fresenius and Will's, iron, chloride of lime, and Bunsen methods. Improved apparatus for Bunsen process (*J. S. C. I.*, 1889, 307, and 1894, 979 and 1221).
513. PATTINSON (*C. N.*, xxi., 267).—The high percentage of available oxygen given by Fresenius and Will's process is not generally due to  $\text{FeO}$ . Describes a modified iron method.
514. LUNGE (*J. S. C. I.*, 1882, 93).—Discusses and answers Fresenius' criticisms of the  $\text{FeSO}_4$  method.
515. DARTON (*J. S. C. I.*, 1882, 468).—Modified Fresenius process :  $\text{CO}_2$  passed into  $\text{Ba}(\text{HO})_2$  and excess titrated with  $\text{HNO}_3$ .
516. PAUL (*C. N.*, xxi., 16).—Dissolve ore along with oxalic acid in  $\text{H}_2\text{SO}_4$  ; titrated with permanganate.
517. HARVEY (*C. N.*, xlvii., 2).—Heats with  $\text{SnCl}_2$  and  $\text{HCl}$ , and estimates excess  $\text{SnCl}_2$  with  $\text{Fe}_2\text{Cl}_6$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ .
518. CHARPENTIER (*C. N.*, lii., 86).—Pass liberated Cl into  $\text{FeSO}_4$  ;  $\text{KCNS}$  and standard  $\text{KHO}$  added until solution is decolourized. Or collect Cl collected in  $\text{AgNO}_3$ , add drop  $\text{Fe}(\text{NO}_3)_3$ , and titrate with  $\text{KCNS}$ . The reaction sensitive to 1/3,000,000.
519. LUNGE (*J. C. S.*, lviii., 1470).—Ore decomposed according to the equation—  

$$\text{MnO}_2 + \text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 = \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{O}_2 ;$$
the O is measured in the nitrometer. (See 430.)
520. CARNOT (*C. N.*, lxviii., 15 and 301).—The oxide reacts with a nitric solution of  $\text{H}_2\text{O}_2$ , and the evolved O is measured. JONES (*C. N.*, lxviii., 305) draws attention to previous proposals, and also to the fact that higher oxides of Pb may be similarly estimated.

*d. Indirect Processes for Estimating Manganese :*

521. RILEY (*C. N.*, xxxv., 175).—Dissolve spiegel in dilute  $\text{H}_2\text{SO}_4$  ; allow 5 per cent. for C, etc. ; difference, Mn. Results low, owing to soluble

organic matter; obviated by taking nitric acid solution to dryness, dissolving in HCl, and reducing with  $\text{Na}_2\text{SO}_3$ . Methods of Parry and Galbraith (487 and 488) are undesirable ones.

522. HOLDICH (*C. N.*, xlix., 9).—As Riley; but recommends a subtraction of determined Si.
523. ATKINSON (*C. N.*, xlix., 25).—Subtracts Fe and Si+6 per cent. for ferro-manganese. Results not so regular as with spiegels.
524. PARRY (*C. N.*, lxvii., 296).—Allows 6 per cent. for spiegel and 7 per cent. for ferro-manganese.
525. TROILIUS (*J. I. S. I.*, 1883, 784).—7.5 per cent. allowed for impurities if Fe is less than 20 per cent.; 6.5 if Fe is 20 to 45 per cent.; 6.0 per cent. if Fe is 45 to 65 per cent.; and 5.5 per cent. for upwards of 65 per cent. Fe. These are Ledebur's figures.
526. DIEHL (*J. C. S.*, l., 101).—Mn and Fe are precipitated with Br and  $(\text{NH}_4)\text{HO}$ ; ignited; Fe determined volumetrically, Mn by difference.

*c. Miscellaneous Volumetric Processes:*

527. LEISON (*C. N.*, xxii., 210).—Mn completely precipitated as oxalate; estimated by titration with permanganate. The separation of metals as oxalates is discussed by Luckow (*C. N.*, lv., 73). (See 328.)
528. BLUM (*J. S. C. I.*, 1891, 798).—Boiling ammoniacal solution containing Mn, Fe,  $(\text{NH}_4)\text{Cl}$ , and tartaric acid is titrated with ferrocyanide; acetic acid used as indicator.
529. MOLDENHAUER (*J. S. C. I.*, 1890, 108).—MnO run into ferro-cyanide until a test with  $\text{CuSO}_4$  paper gives no red colour.
530. NASS (*J. C. S.*, lxvi., 1482).—Classen's process (328) useless for estimating Mn, Co, or Ni.
531. NEUMANN (*C. N.*, lxxii., 212).—Neutral solution precipitated with alkaline sulphide; excess of sulphide estimated. Process applied to a dozen other metals.
532. ROSSLER (*C. N.*, xl., 169).—MnO solution, free from halogens and organic matter, mixed with standard Ag solution; Ag precipitated with sodium carbonate; excess  $(\text{NH}_4)\text{HO}$  added; filtrate titrated with KCNS. A similar process for cobalt (*C. N.*, xli., 184).
533. PURGOTTI (*J. C. S.*, lxxii., ii., 349).— $\text{MnO}_2$  reacts with hydrazine sulphate to form N, which is measured at N. T. P. Per cent. Mn calculated from this.

**V. Detection of Manganese.**

534. BOTTGER (*C. N.*, xxiv., 192).—Fragment of the substance, dropped into fused  $\text{KClO}_3$ . Peach-blossom red indicates Mn.
535. HILLEBRAND (*C. N.*, lxxviii., 80).—During alkaline fusion an oxidizing atmosphere must be in the crucible, otherwise negative results are obtainable when Mn is present.
536. VITALI (*J. C. S.*, lxxvi., ii., 251).—Add  $\text{H}_2\text{SO}_4$  and  $\text{BrO}_3$ ; a red violet colour = Mn.

## VI. Miscellaneous Notes.

537. KERN (*C. N.*, xxxviii., 268).—Mn unequally distributed in alloys. A difference of 2·2 per cent. observed.
538. CARNOT and GOUTAL (*J. C. S.*, lxxii., ii., 555).—If in small quantity, Mn is present in iron as silicide or sulphide. In larger amounts, it is either partly dissolved or in combination with the iron.
539. LEDEBUR (*J. I. S. I.*, 1884, 269).—Compares Volhard, chlorate, and Pattinson processes. In  $\text{KClO}_3$  process the precipitated solution was heated near boiling-point for two hours; results 0·5 to 1·0 per cent. too low; very difficult to wash free from  $\text{KClO}_3$ . Pattinson's process most meritorious, but Cu, Co, and Ni cause plus errors.
540. SANITER (*J. S. C. I.*, 1894, 112).—Reviews Pattinson, Volhard, pyrophosphate, and  $\text{Mn}_3\text{O}_4$  methods. Proposed to precipitate as sulphide before ignition to  $\text{Mn}_3\text{O}_4$ ; if precipitated as  $\text{Mn}(\text{HO})_2$  not reliable.
541. RURUP (*J. I. S. I.*, 1896, i., 534).—Examines estimation as sulphide,  $\text{Mn}_3\text{O}_4$ ; chlorate process (Ford's), weighing as  $\text{Mn}_3\text{O}_4$ ; Volhard's, separation of Fe with  $\text{Na}_2\text{SO}_4$ , and titrating with  $\text{KMnO}_4$ ; and the  $\text{KClO}_3$  volumetric process. All accurate for steel works' purposes.
542. JUPTNER (*J. I. S. I.*, 1895, i., 507).—Draws attention to various atomic weight values as a cause of differences.
543. HOGG (*C. N.*, lxviii., 163).—Cyano-nitride of titanium occurs in all high-grade spiegels and ferro-manganeses. In the latter, half a million separate crystals are calculated to occur in each cubic inch; they are separated by elutriating the nitric acid residue.

## SULPHUR.

The following arrangement of the means of estimating sulphur is far from perfect, but, on the whole, it groups similar processes into the same section better than some other arrangements which have been suggested. In each section the items are arranged, as far as possible, with respect to the estimation of sulphur in metals, in fuels (solid), and in compounds containing higher percentages of sulphur (pyrites, etc.). Many processes may be used for either metals, fuels, or pyrites; these are placed in that connection where they are most commonly used. The arrangement is:

- I. OXIDATION TO SULPHURIC ACID, WITH—
  - a.* Gravimetric Estimation.
  - b.* Volumetric Estimation.
- II. EVOLUTION AS SULPHURETTED HYDROGEN, WITH—
  - a.* Gravimetric Estimation.
  - b.* Volumetric Estimation.
- III. MISCELLANEOUS ITEMS.

### Oxidation to Sulphuric Acid.

#### *a. Gravimetric Estimation.—*

- 544. LEFORT (*C. N.*, xix., 132).—One part HCl to three parts HNO<sub>3</sub> is the most suitable proportion of these acids for the rapid oxidation of sulphur.
- 545. NICKLES (*C. N.*, vii., 87).—The iron is dissolved in bromine; the S precipitated as BaSO<sub>4</sub>.
- 546. NOYES and HELMER (*J. S. C. I.*, 1901, 1143).—Best solvents are dilute Br or HNO<sub>3</sub> + KBr + KClO<sub>3</sub>. Fe precipitated with (NH<sub>4</sub>)HO and S estimated in filtrate.
- 547. TOSH (*C. N.*, xvi., 168).—Dissolve in HNO<sub>3</sub> with a little HCl, evaporate, re-dissolve in HCl, and add BaCl<sub>2</sub>.
- 548. EGGERTZ (*C. N.*, xvii., 207).—To solution of KClO<sub>3</sub> containing the iron, add HCl, evaporate, filter, and add BaCl<sub>2</sub> to nearly neutral solution. A similar process for iron minerals containing either Ba, Sr, or Pb.
- 549. PIESSE (*C. N.*, xxviii., 248).—Dissolve in aqua regia, evaporate nearly dry, take up in HCl, and add BaCl<sub>2</sub>. WILLIAMS (*C. N.*, xxviii., 266).—Same process, but dissolves in 1.20 HNO<sub>3</sub>.
- 550. ALLEN (*C. N.*, xxix., 91 and 112).—HCl retards, if it does not altogether prevent, the precipitation of BaSO<sub>4</sub>; neutralize the iron solution as far as possible with ammonia, and put aside for twenty-four hours. (See 555.)



551. PLATZ (*J. I. S. I.*, 1887, i., 471).—Dissolve in 1·18  $\text{HNO}_3$ , evaporate with  $\text{HCl}$ , etc. The  $\text{BaSO}_4$  and wet filter are ignited at low temperature, and then more strongly to oxidize any sulphide to sulphate. (See 568).
552. REIS (*J. I. S. I.*, 1889, ii., 479).—When iron is dissolved in  $\text{HNO}_3$ , sulphur escapes estimation as  $\text{H}_2\text{S}$  and  $\text{S}$ . (See 646).
553. AUCHY (*J. S. C. I.*, 1901, 620).—Minimises loss of  $\text{S}$  by dissolving in aqua regia slowly. Add  $\text{BaSO}_4$ , boil 30 minutes and settle overnight. Make a positive correction.
554. PARRY and MORGAN (*C. N.*, lxxvii., 247).—Dissolve in aqua regia, evaporate three or four times with  $\text{HCl}$  to expel  $\text{HNO}_3$ , dilute faintly  $\text{HCl}$  solution to 700 c.c., and add  $\text{BaCl}_2$ .  $\text{BaSO}_4$  is soluble in acid  $\text{Fe}_2\text{Cl}_6$ . Or evolve as  $\text{H}_2\text{S}$ , absorb in  $\text{CuSO}_4$ , and ignite precipitate to  $\text{CuO}$  (see 669).  $\text{S}$  may be retained by the  $\text{H}_2\text{SO}_4$  liquor and the insoluble residue.
555. ARCHBUTT (*J. S. C. I.*, 1890, 25).—In the aqua regia process,  $\text{BaSO}_4$  should be precipitated from the concentrated solution; precipitation is complete in two hours, and excess of  $\text{HCl}$  does no harm. (See 625).
556. ANON (*J. I. S. I.*, 1893, i., 410).—The nitro-hydrochloric process is subject to error, through formation of basic salts before filtering off  $\text{SiO}_2$  or during precipitation of  $\text{BaSO}_4$ , and precipitating  $\text{BaSO}_4$  from too acid a solution.
557. BAMBER (*J. I. S. I.*, 1894, i., 319).—Dissolve metal in  $\text{HNO}_3$ , add  $\text{Na}_2\text{CO}_3$  short of alkalinity, evaporate, roast, extract with dilute  $\text{Na}_2\text{CO}_3$ , and precipitate as  $\text{BaSO}_4$ .
558. PHILLIPS (*C. N.*, lxxii., 239).— $\text{S}$  in  $\text{Cu}$  is estimated by precipitating as  $\text{BaSO}_4$  from  $\text{CuCl}_2$  solution;  $\text{BaSO}_4$  is soluble in  $\text{Cu}(\text{NO}_3)_2$ . Precautions taken against contamination of the  $\text{BaSO}_4$  with  $\text{AgCl}$  or  $\text{PbSO}_4$ .
559. BRUYN (*J. C. S.*, lxxii., 753) and HEATH (*J. S. C. I.*, 1896, 218).—Dissolve  $\text{Cu}$  in  $\text{HNO}_3$ , precipitate electrolytically, and estimate  $\text{S}$  in the  $\text{Cu}$ -free liquor.
560. HAMPE (*J. S. C. I.*, 1891, 486).—Estimate  $\text{S}$  in  $\text{Pb}$  by adding filings to molten  $\text{KNO}_3$ , passing  $\text{CO}_2$  through water solution to precipitate  $\text{Pb}$ , and adding  $\text{BaNO}_3$  to the filtrate.
561. CAMPBELL (*C. N.*, lv., 74).—Boil soluble slag with  $\text{HCl}$  and  $\text{Br}$ , and precipitate nearly neutralized filtrate with  $\text{BaCl}_2$ .
562. ATKINSON (*J. I. S. I.*, 1896, ii., 207).—Roast powdered ore, short of fusion, with  $\text{Na}_2\text{CO}_3$ , raising the temperature gradually, dissolve out  $\text{Na}_2\text{SO}_4$ , and precipitate as  $\text{BaSO}_4$ .
563. PHILLIPS (*C. N.*, lxxv., 194).—By fusion of powdered irons with  $\text{Na}_2\text{O}_2$  a higher percentage is obtained than by oxidation with acids. The interference of organic sulphur compounds with evolution processes.
564. MEINECKE (*C. N.*, lix., 107), BOUCHER (*C. N.*, lxxiv., 76), and CARNOT and GOUTAL (*J. C. S.*, lxxii., ii., 520).—Decompose  $\text{Fe}$  with acid cuprammonium chloride at boiling-point, oxidize filtered residue with aqua regia and  $\text{KClO}_3$  or  $\text{Br}$  and  $\text{HCl}$ , and precipitate as  $\text{BaSO}_4$ .

565. TAMM (*J. I. S. I.*, 1887, ii., 369).—On account of solubility of  $\text{BaSO}_4$  in  $\text{Fe}_2\text{Cl}_6$ , add  $\text{BaCl}_2$ , evaporate, fuse impure  $\text{BaSO}_4$  with  $\text{Na}_2\text{CO}_3$ , and reprecipitate. Wiborgh's (710) is more accurate than Eggertz's (707) colour process.
566. REIS (*J. I. S. I.*, 1889, i., 396).—Heat metal with  $\text{MgO}$  and  $\text{NaHO}$ , leach, filter, and boil with  $\text{BaCl}_2$ .
567. MEINECKE (*J. C. S.*, lxxvi., ii., 518).—Dissolve the pig in  $\text{HCl}$  and  $\text{KClO}_3$ , expel  $\text{Cl}$ , reduce  $\text{Fe}$  with  $\text{Zn}$ , and add  $\text{BaCl}_2$ .
568. BOUSSINGAULT (*C. N.*, xv., 324).— $\text{BaSO}_4$  ( $\text{CaSO}_4$ ,  $\text{PbSO}_4$ , etc.) is decomposed at high temperatures, and therefore should not be unduly heated.
569. MARSH (*C. N.*, lix., 309).—Appreciable amounts of  $\text{BaSO}_4$  are reduced by the carbon of the filter-paper. Precipitate should be treated with  $\text{H}_2\text{SO}_4$ , and again ignited.
570. RIPPER (*J. C. S.*, lxiv., ii., 239).—Oxidizes sulphate reduced by the paper with  $\text{H}_2\text{SO}_4$  and  $\text{Br}$ , and removes other impurities by digesting with  $\text{HCl}$  and  $\text{Br}$ . (See 664).
571. MARBOUTIN (*C. N.*, lxxvi., 232).—By igniting  $\text{BaSO}_4$  filter apex upwards no sulphides are formed.
572. FOULK (*J. C. S.*, lxxii., 189).—Acid solutions need an excess of  $\text{BaCl}_2$  to completely precipitate the  $\text{S}$ . The moist filter is ignited apex up.
573. SLEEPER (*C. N.*, lxix., 63).— $\text{BaSO}_4$  does not carry  $\text{SiO}_2$  down with it.  $\text{SiO}_2$  can be volatilized from  $\text{BaSO}_4$  if free  $\text{H}_2\text{SO}_4$  is present also.
574. RICHARDS and PARKER (*C. N.*, lxxii., 281).—The occlusion of  $\text{BaCl}_2$  by  $\text{BaSO}_4$  increases with concentration and the presence of  $\text{HCl}$ . Results corrected by estimating  $\text{Cl}$  in the precipitate and deducting equivalent amount of  $\text{BaCl}_2$ .
575. SLOANE (*C. N.*, xliv., 221).—The various means of purifying  $\text{BaSO}_4$  precipitates, and objections to them.
576. ZIEGLER (*J. I. S. I.*, 1882, 384).—Add  $\text{AgNO}_3$ , after  $\text{BaCl}_2$  to facilitate and complete the precipitation of  $\text{BaSO}_4$ ; wash filter with  $\text{AmHO}$  to remove  $\text{AgCl}$ .
577. JANNASCH and RICHARDS (*C. N.* lx., 19).— $\text{BaSO}_4$  is insoluble in cold ferric solutions. A portion of the iron is always precipitated as barium-ferric sulphate [Schneider, (*J. I. S. I.*, 1893, i., 409), disputes this], which is decomposed with loss of  $\text{SO}_3$ , on ignition. Organic acid does not prevent this contamination (see 587 and 630, and Richards, *C. N.*, lxxxi. 185).
578. AULICH (*J. I. S. I.*, 1899, ii., 486).—Resumé of the processes for preventing contamination of  $\text{BaSO}_4$  with  $\text{Fe}$ .
579. MEINECKE (*J. I. S. I.*, 1899, ii., 490) and HEIDENREICH (*J. C. S.*, lxxvi., ii., 517).—To prevent iron accompanying  $\text{BaSO}_4$ , reduce to  $\text{FeO}$  with zinc before precipitating.
580. HERTING (*J. C. S.*, lxxvi., ii., 804).—Reduce to  $\text{FeO}$  with  $\text{SnCl}_2$ , before adding  $\text{BaCl}_2$ .

581. NOAILLON (*J. S. C. I.*, 1901, 934).—Results too high when precipitated from  $\text{Al}_2\text{Cl}_6$  solution; error negligible if 5 per cent. free  $\text{HCl}$  is present.
582. FRESSENIUS and HINTZ (*C. N.*, lxxiii., 276).—Particulars of the solubility of  $\text{BaSO}_4$  with excess of  $\text{BaCl}_2$  or  $\text{H}_2\text{SO}_4$  in water, alkaline chloride,  $\text{HCl}$ , and  $\text{HNO}_2$  solutions.
583. MORGAN (*C. N.*, lviii., 63 and 75).—Reviews some well-known objections to the methods based on oxidation and precipitation as  $\text{BaSO}_4$  and evolution as  $\text{H}_2\text{S}$ .
584. SPILLER (*C. N.*, x., 219).—Glacial  $\text{H}_3\text{PO}_4$  and pyrophosphate interfere with the precipitation of  $\text{BaSO}_4$ .
585. CROSSLEY (*C. N.*, v., 245).—When S is oxidised by evaporation with  $\text{HNO}_3$ , an alkaline salt must be added to prevent  $\text{SO}_3$  being volatilized.
586. J. T. (*C. N.*, lxxviii., 294).—The blank of the acids used should be found by treating two samples (one half the weight of the other) in the usual way, and deducting the  $\text{BaSO}_4$  of the larger from twice the  $\text{BaSO}_4$  of the smaller sample.

*Sulphur in Fuels.*

587. STORER (*C. N.*, xxi., 196).—Coal, pyrites, or free S may be oxidized by heating with  $\text{HNO}_3 + \text{KClO}_3$ . The  $\text{BaSO}_4$  is precipitated from tartaric solutions, and washed with  $\text{Am}\bar{\text{A}}$  to remove adherent  $\text{Ba}(\text{NO}_3)_2$ .
588. BRADBURY (*C. N.*, xxxviii., 147).—Part of the sulphur in coal, *i.e.*, that organically combined, is not oxidized to  $\text{H}_2\text{SO}_4$  by treatment with acids.
589. DROWN (*C. N.*, xliii., 89).—By separate treatment with  $\text{NaHO}$ ,  $\text{Br}$ , and  $\text{HCl}$ , S existing as pyrites or soluble sulphate is dissolved; that organically combined, not. For total S, burn in O, absorb gases in  $\text{KMnO}_4$ , and fuse the residue.
590. WALLACE (*C. N.*, xli., 201).—Sulphur *must* exist organically combined when no sulphates are present, and not nearly enough iron to form the bisulphide.
591. HELM (*J. I. S. I.*, 1882, 345).—Gaseous and liquid S compounds are evolved from coal at a temperature below the decomposition of  $\text{FeS}_2$  or the volatilization of S, and therefore part of the sulphur is organically combined.
592. MUCK (*J. I. S. I.*, 1886, 866).—Evidence that S in coal may be organically combined. The coal containing least sulphur does not necessarily produce the purest coke.
593. BLUM (*C. N.*, lviii., 65).—Wet oxidations remove only such S as is combined with Fe or Ca. Total S obtained by fusion with  $\text{KNO}_3 + \text{NaCl} + \text{Na}_2\text{CO}_3$ .
594. GRITTNER (*J. C. S.*, lxiv., ii., 89).—Estimates S in coal ash by treating with  $\text{Br}$  and  $\text{HCl}$ , precipitating Fe with  $\text{AmHO}$ , and adding  $\text{BaCl}_2$ . This amount subtracted from "total" gives "combustible S."

595. CALVERT (*C. N.*, xxiv., 76).— $\text{CaSO}_4$  should be distinguished from  $\text{FeS}_2$  in coal analysis. Boil with  $\text{H}_2\text{O}$ , estimate  $\text{CaSO}_4$  in filtrate, oxidize residue with aqua regia, and fuse dried mass with  $\text{Na}_2\text{CO}_3$ .  $\text{HNO}_3$  prevents precipitation of  $\text{BaSO}_4$ . In the direct oxidation with aqua regia, sub-sulphate of iron becomes firmly attached to the carbonaceous mass.
596. REICHERT (*C. N.*, xxi., 35).—Ignite charcoal with  $\text{KNO}_3$ ; estimate S as usual.
597. A. A. (*C. N.*, xxiii., 30).—Add powdered coke to fused  $\text{KClO}_3$  or  $\text{KNO}_3$ , and precipitate acidified solution with  $\text{BaCl}_2$ .
598. NAKAMURA (*C. N.*, xl., 237).—Heat with mixed alkaline carbonates over a spirit-lamp. Precipitate as usual.
599. ASBOTH (*J. C. S.*, lxx., ii., 448) and GLASER (*J. C. S.*, lxxiv., ii., 483).—Fuse with  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{O}_2$ , boil acidified solution with Br, and precipitate as  $\text{BaSO}_4$ .
600. ATKINSON (*J. S. C. I.*, 1886, 154).—As in 562. By heating pyrites with  $\text{Na}_2\text{CO}_3$ , not more than 96 per cent. of the S is retained. (See 644.)
601. STOLBA (*J. S. C. I.*, 1888, 524).—Mix with equal amounts of Ag powder and  $\text{KHCO}_3$ , heat residue with  $\text{AmNO}_3$ , and precipitate as usual.
602. STOCK (*C. N.*, xxx., 211).—Mix coal to paste with  $\text{CaO}$ , ignite, add  $\text{AmNO}_3$ , re-ignite, dissolve in  $\text{HCl}$ , and add  $\text{BaCl}_2$ . KONINCK and NIHOUL (*J. C. S.*, lxviii., ii., 136) use  $\text{CaO} + \text{Ca}(\text{NO}_3)_2$ .
603. ESCHKA (*C. N.*, xxxi., 261).—Heat powdered fuel with  $\text{Na}_2\text{CO}_3 + \text{MgO}$ , re-heat with  $\text{AmNO}_3$ , leach and precipitate S.
604. ROTHE (*J. S. C. I.*, 1891, 952).—The roasting of 603 may be done in porcelain crucibles with less danger of S contamination from the gas.
605. HUNDESHAGEN (*C. N.*, lxvi., 169; and lxviii., 49).—By using  $\text{K}_2\text{CO}_3 + \text{MgO}$  instead of Eschka mixture (603) the combustion is more rapid and the loss as  $\text{H}_2\text{S}$  obviated; this applies to fuels rich in volatile S.
606. HANDY and CAMP (*C. N.*, lxvii., 90).—Hundeshagen's modification is no improvement on the original.
607. PATTINSON (*C. N.*, xxxix., 30).—As 602, omitting  $\text{AmNO}_3$  treatment. Determines total S and S in ash. Also PELLET (*J. C. S.*, lxxx., ii., 622).
608. ANTONY and LUCCHESI (*J. I. S. I.*, 1899, ii., 492) and DUBOIS (*J. S. C. I.*, 1901, 1241).—Heat with  $\text{MnO}_2 + \text{KMnO}_4 + \text{Na}_2\text{CO}_3$ , acidulate with  $\text{HNO}_3$ , and precipitate as  $\text{BaSO}_4$ . As accurate as 603, and quicker.
609. PRUNIER (*J. C. S.*, lviii., 290).—Heat with  $\text{KMnO}_4$ , pass gases into  $\text{KMnO}_4$ , digest residue with water, add to absorbing  $\text{KMnO}_4$ , and treat with  $\text{HCl}$  and  $\text{BaCl}_2$ .
610. NEILSON (*C. N.*, lxiii., 192).—Fuse coke with  $\text{Na}_2\text{CO}_3$  and  $\text{MnCO}_3$ , evaporate with  $\text{HCl}$ , and precipitate as  $\text{BaSO}_4$ . Compares with  $\text{CaO}$ ,  $\text{MgO}$ , and alkaline fusion processes.
611. MIXTER (*C. N.*, xxvii., 53; and xlvi., 217).—Burn substances in O and condense  $\text{H}_2\text{SO}_4$  from the gaseous products. Elaborate apparatus, but process widely applicable. A description of Sauer's process.

612. SAUER (*C. N.*, xxviii., 226).—Burn in O, absorb  $\text{SO}_2$  in bromized HCl. See also MARCHLEWSKI (*J. C. S.*, lxiv., ii., 551).
613. BERTHELOT (*J. C. S.*, lviii., 1462).—Burn with O at 25 atmospheres in a calorimetric bomb; the S is converted to  $\text{H}_2\text{SO}_4$ .
614. HEMPEL (*J. C. S.*, lxiv., ii., 187).—Burn the coal electrolytically in a glass bottle, complete oxidation with Br, and precipitate with  $\text{BaCl}_2$ .
615. BRUHLE (*J. S. C. I.*, 1889, 219).—Heat mixture of coal and oxidant in a covered boat to prevent escape of  $\text{SO}_2$ . Results higher than by open fusion.
616. BAILEY (*J. C. S. I.*, 1889, 360).—Imperfections of various methods; prefers 603.

*Sulphur in Pyrites, etc.*

617. YARDLEY (*C. N.* xxv., 257).—Pyrites oxidized at high temperatures with  $\text{HNO}_3$  do not lose  $\text{H}_2\text{SO}_4$ , but low temperatures are more favourable both to the decomposition of the ore and the precipitation of the  $\text{BaSO}_4$ .
618. LUNGE and BRODENRIG (*C. N.*, xlviii., 285; and lxi. 76).—In opening pyrites with aqua regia,  $\text{HNO}_3$  not stronger than 1.42 should be used. Oxidize with Br and  $\text{HNO}_3$ , and separate Fe by pouring into  $\text{AmHO}$ ; the excess must not be boiled off or basic ferric sulphates form.
619. WÖHLER (*C. N.*, xviii., 72).—Pyrites suspended in water is completely dissolved on passing hypochloric acid.
620. JOHNSON (*C. N.*, lxx., 212).—Decompose pyrites with  $\text{HNO}_3$  and  $\text{KClO}_3$ , reduce Fe in HCl solution with hypophosphite (which also destroys traces of  $\text{HNO}_3$ ), and precipitate with  $\text{BaCl}_2$ .
621. STANSBIE (*C. N.*, lxxiv., 189).—Oxidize the sulphide (or even pure S) with  $\text{HNO}_3$  and Br. Or heat with CaO; precipitate S as usual.
622. WESTMORELAND (*J. S. C. I.*, 1887, 84).—Lunge's old and new methods give like results. Only small excess of  $\text{BaCl}_2$  should be used and HCl used sparingly in the washing.
623. LUNGE (*J. S. C. I.*, 1887, 96).—Galena does not materially interfere when pyrites is opened out with aqua regia.
624. NOAILLON (*J. C. S.*, lxii., ii., 595).—Oxidize mineral sulphides with  $\text{HNO}_3 + \text{NaClO}_3$ , evaporate with HCl, and finish as in 618.
625. TESCHEMACHER and SMITH (*C. N.*, xxiv., 61, etc.).—Precipitated  $\text{BaSO}_4$  carries down K, Ba, Cu, Mg, Fe, etc.; it is noticeably soluble in dilute HCl and  $\text{HNO}_3$ , and ignited over gas is considerably reduced. Decompose pyrites and titrate HCl solution as in 641.
626. GLENDINNING and EDGAR (*C. N.*, xxiv., 140; and xxvii., 13).—Solubility of  $\text{BaSO}_4$  in HCl exaggerated in 625. Gravimetric estimation of S in pyrites a reliable process. Great discrepancies may arise from grinding the mineral in wedgwood or porcelain mortars.
627. GLADDING (*C. N.*, lxx., 181).—Nitrates cause high results; chlorides cause no error. Results low through Fe being precipitated as ferric sulphate. When Fe is precipitated with  $\text{AmHO}$ , a little S remains with

- the  $\text{Fe}_2(\text{HO})_6$ . Oxidize pyrites with  $\text{HNO}_3$  and Br.  $\text{BaSO}_4$  is insoluble in  $\text{Fe}_2\text{Cl}_6$ .
628. LUNGE (*C. N.*, lxxi., 132).—There is no advantage in 627 so far as it professes to be a modification of 618.  $\text{BaSO}_4$  is distinctly soluble in acid  $\text{Fe}_2\text{Cl}_6$ . Process 620 is unworkable.
629. GLADDING (*J. C. S.*, lxx., ii., 622 and 672).—If  $\text{BaCl}_2$  be not added in drops, it contaminates the  $\text{BaSO}_4$ . Lunge contends that it makes no practical difference how the  $\text{BaCl}_2$  is added.
630. KÜSTER and THIEL (*J. C. S.*, lxxvi., ii., 247 and 805; and lxxviii., ii., 242).—Prevent Fe contaminating  $\text{BaSO}_4$  by adding oxalate or tartrate (see 577); or precipitate Fe with  $\text{AmHO}$ , add  $\text{BaCl}_2$ , and then redissolve the  $\text{Fe}_2(\text{HO})_6$  with  $\text{HCl}$ .
631. MACAGNO (*C. N.*, xliii., 192).—Digest S ore with a known amount of  $\text{CS}_2$ , determine its specific gravity, and read off the amount of S dissolved from tabulated observations.
632. SMITH (*C. N.*, lxii., 206).—Sulphides are oxidized to  $\text{H}_2\text{SO}_4$  by mixing with molten  $\text{KHO}$  and passing electric current.  $\text{BaSO}_4$  precipitated in a solution free from Fe, etc.
633. REICHARDT (*C. N.*, xlii., 259).—Iron and copper pyrites are oxidized with Br water.
634. LUNGE (*C. N.*, xl., 184).—Dry processes attack both galena and heavy spar, and this partly accounts for the results being higher than by the wet processes.
635. GLASER (*C. N.*, lxx., 179), CLARK (*J. C. S.*, lxiii., 1080), and ASBOTH (*J. C. S.*, lxx., ii., 71).—Fuse with  $\text{Na}_2\text{O}_2$ , add  $\text{HBr}$ , acidify, boil off Br and add  $\text{BaCl}_2$ .
636. DEUTECOM (*C. N.*, xlii., 317) and BOCKMANN (*C. N.*, xlv., 95).—Decompose with  $\text{Na}_2\text{CO}_3 + \text{KClO}_3 + \text{NaCl}$ ; precipitate as usual.
637. CLARK (*J. S. C. I.*, 1885, 329, 573, and 724).—Heat powdered pyrites with  $\text{MgO} + \text{NaHO}$ , precipitate Pb with  $\text{CO}_2$ , acidify, and add  $\text{BaCl}_2$ .
638. KELLER and MAAS (*J. C. S.*, lxx., ii., 498).—Copper pyrites and roasted ores are opened up with  $\text{KHO}$  and  $\text{Na}_2\text{O}_2$ .
639. JANNASCH (*C. N.*, lxi., 114 and 124).—Heat in bromized air and absorb gases in  $\text{HCl}$  and tartaric acid. Br may be replaced by  $\text{HNO}_3$ . Later simple ignition in oxygen is preferred. (See 611.)
640. HINDS (*C. N.*, lxxiii., 285).—Measure the height of a column of liquid containing the  $\text{BaSO}_4$  through which a candle flame is just visible. The percentage  $\text{H}_2\text{SO}_4 \times \text{depth of column}$  is a constant. AGLOT (*J. C. S.*, lxxii., ii., 431).—Accurate results can be obtained only in alcoholic solutions.

*b. Volumetric Estimation :*

641. WRIGHT (*C. N.*, xvii., 122).—Oxidize pyritic ore with aqua regia, add small excess  $\text{BaCl}_2$ , and then  $\text{Na}_2\text{SO}_4$  until neither Ba nor  $\text{SO}_3$  is in solution. Other methods of oxidizing the ore; one suitable in case Pb is present.

642. HOLLAND (*C. N.*, xxvii., 15).—A point is reached in 641 when either  $\text{H}_2\text{SO}_4$  or  $\text{BaCl}_2$  will produce a precipitate in the filtered liquid. Pyrites decomposed by fusion in a closed tube carrying a delivery tube.
643. BERINGER (*C. N.*, lix., 41).—The titration of  $\text{H}_2\text{SO}_4$  with  $\text{BaCl}_2$  is best made in an acetic solution containing sodium acetate. A true finishing point is arrived at (642). The interference of many metals observed.
644. PELOUZE (*C. N.*, v., 45).—Heat powdered pyrites with  $\text{Na}_2\text{CO}_3 + \text{KClO}_3 + \text{NaCl}$ . The  $\text{Na}_2\text{CO}_3$  which has not combined (see 600) with the sulphur is titrated. Neither Si, Ba, nor Ca interfere.
645. WATSON (*J. S. C. I.*, 1888, 305).—Heat burnt pyrites with  $\text{Na}_2\text{CO}_3$  alone, and titrate as in 644. Soluble sulphur is determined by boiling with standard  $\text{Na}_2\text{CO}_3$ .
646. LUNGE (*J. S. C. I.*, 1893, 292).—Heat as in 645, short of fusion, and extract with NaCl.  $\text{H}_2\text{S}$  may be evolved from FeS when treated with nitro-hydrochloric acid; oxidize with  $\text{HNO}_3$  and then add HCl. (See 552.)
647. SCHWARZ (*C. N.*, viii., 207).—Add  $\text{PbNO}_3$ , filter off  $\text{PbSO}_4$ , and titrate excess Pb with  $\text{K}_2\text{Cr}_2\text{O}_7$  using  $\text{AgNO}_3$  indicator. PELLET (*C. N.*, xxxiii., 9) used same process, but estimates  $\text{K}_2\text{Cr}_2\text{O}_7$  with  $\text{FeSO}_4$  and  $\text{KMnO}_4$ .
648. CLEMM (*C. N.*, xix., 287), GAWALOWSKI (*C. N.*, lviii., 72), and many others.—To neutral solution add  $\text{BaCl}_2$ , then  $\text{Na}_2\text{CO}_3$  to precipitate excess Ba, and titrate the residue of  $\text{Na}_2\text{CO}_3$  with  $\text{H}_2\text{SO}_4$ . NORTH (*C. N.*, lix., 58).—This process is worthless.
649. JEAN (*C. N.*, xxxiv., 272), HAUBST (*C. N.*, xxxv., 27), GROSSMAN (*C. N.*, xli., 114), and CHERIX, (*J. C. S.*, lxiv., ii., 89).—Add  $\text{Ba}(\text{HO})_2$ , precipitate excess with  $\text{CO}_2$ , and titrate the alkali (which was combined with the  $\text{SO}_3$ ) with standard acid. Ca and Mg do not interfere.
650. FARNSTEINER (*C. N.*, lxvi., 296).—Add  $\text{BaCl}_2$  precipitate excess in faintly ammoniacal solution with  $\text{K}_2\text{CrO}_4$ , and titrate residual  $\text{K}_2\text{CrO}_4$  with iodine. Similar processes, varying chiefly in the means of estimating the final  $\text{K}_2\text{CrO}_4$ , are given by PRECHT (*C. N.*, xli., 24), WINDISH (*J. C. S.*, lxviii., ii., 137), and MARBOUTIN (*C. N.*, lxxvi., 232), and others. Marboutin gives a resumé of volumetric processes for estimating S.
651. QUANTIN (*C. N.*, liv., 233).—Add excess of an HCl solution of  $\text{BaCrO}_4$ ;  $\text{SO}_3$  replaces  $\text{CrO}_3$ ; precipitate excess  $\text{BaCrO}_4$  with  $\text{AmHO}$ , and titrate the  $\text{CrO}_3$  equivalent to the  $\text{SO}_3$  with  $\text{FeSO}_4$ . Processes on the same principle are given by STOLLE (*J. C. S.*, lxiv., ii., 188), REUTER (*J. C. S.*, lxxvi., ii., 53), BAUMANN (*J. C. S.*, lxi., 104), and ANDREWS (*J. C. S. I.*, 1890, 328).
652. ASBOTH (*C. N.*, lxvi., 168).—The HCl solution of  $\text{BaCrO}_4$  (651) is gradually decomposed, and is reliable only when freshly made.
653. SOLTSEIN (*J. C. S.*, lx., 115).—Add  $\text{BaCl}_2$ , and titrate excess with  $\text{K}_2\text{Cr}_2\text{O}_7$ , using hæmatoxylin or logwood as indicator.



654. FREUND (*J. C. S.*, lxii., 1377).—Add excess  $\text{BaHPO}_4$ , remove  $\text{BaSO}_4$ , precipitate  $\text{Ba}_3(\text{PO}_4)_2$  with  $\text{Na}_2\text{CO}_3$ , dissolve precipitate in  $\text{HCl}$ , add  $\text{Na}_2\text{SO}_4$ , and titrate  $\text{H}_3\text{PO}_4$  in the filtered liquid on the principle that, to methyl-orange the acid is mono, and to phenolphthalein it is bibasic.
655. MARCHLEWSKI (*J. S. C. I.*, 1893, 375 ; and 1894, 283).—Comparative tests and criticism of various oxidation and evolution methods. Andrew's process (651) can be used in the presence of  $\text{Mg}$ ,  $\text{Ca}$ ,  $\text{Al}$ ,  $\text{Zn}$ ,  $\text{Fe}$ ,  $\text{Ni}$ ,  $\text{Co}$ , and  $\text{Ag}$ .
656. COLSON (*C. N.*, xl., 205), and BURTON (*J. S. C. I.*, 1890, 330).—Burn in oxygen, and titrate  $\text{SO}_2$  which has been collected in  $\text{NaHO}$ .
657. NABERY (*J. I. S. I.*, 1896, ii., 456).—As in 656 for coals ; titrate excess  $\text{NaHO}$  with  $\text{H}_2\text{SO}_4$ . Very little  $\text{S}$  remains with the ash.

## II. Evolution as Sulphuretted Hydrogen.

### a. Gravimetric Estimation :

658. ABEL (*C. N.*, vi., 124).—Dissolve  $\text{Fe}$  in strong  $\text{HCl}$ , absorb  $\text{H}_2\text{S}$  in  $\text{Pb}\bar{\text{A}}_2$ , and convert  $\text{PbS}$  into and weigh as  $\text{PbSO}_4$ .
659. FORBES (*C. N.*, xvi., 105).—Digest with cold  $\text{HCl}$ , pass  $\text{H}_2\text{S}$  into ammoniacal  $\text{ZnCl}_2$ , boil with  $\text{HNO}_3$ , and precipitate as  $\text{BaSO}_4$ .
660. HAMILTON (*C. N.*, xxi., 147).—Absorb  $\text{H}_2\text{S}$  in  $\text{KHO}$ , oxidize with chlorine, and add  $\text{BaCl}_2$ . Oxidize residue with aqua regia, and collect small amount of precipitated  $\text{BaSO}_4$ .
661. REINHARDT (*J. I. S. I.*, 1885, 650).—Absorb in  $\text{KHO}$ , oxidize with  $\text{Br}$  and  $\text{HCl}$  ; or absorb in alkaline  $\text{PbO}$ , and convert  $\text{PbS}$  to  $\text{PbSO}_4$ . (*J. C. S.*, lviii., 1464).— $\text{NaHO}$  is used containing a known amount of  $\text{H}_2\text{SO}_4$  in order to assist the collection of the  $\text{H}_2\text{SO}_4$  from the iron.
662. DROWN (*C. N.*, xxix., 201).—Absorb  $\text{H}_2\text{S}$  in permanganate, decompose the  $\text{KMnO}_4$  with  $\text{HCl}$ , and add  $\text{BaCl}_2$ .
663. PETER (*J. I. S. I.*, 1885, 618).—As 662 ; using concentrated  $\text{KMnO}_4$ , and applies the process to ferro-silicon.
664. SCHNEIDER (*J. I. S. I.*, 1893, ii., 532).—Permanganate the best absorbent for  $\text{H}_2\text{S}$  ; neither the residue nor the solution of the metal contains  $\text{S}$ . The treatment of ferriferous  $\text{BaSO}_4$  with  $\text{HCl}$  only makes bad results worse.
656. AUCHY (*J. I. S. I.*, 1896, ii., 445).—Absorb  $\text{H}_2\text{S}$  in alkaline  $\text{KMnO}_4$ , decompose with  $\text{HCl}$  and oxalic acid, and precipitate as  $\text{BaSO}_4$ . Determine  $\text{S}$  in the evolution flask residue.
666. KONINCK (*C. N.*, xxiii., 204).—Collect in  $\text{AgNO}_3$ , digest  $\text{Ag}_2\text{S}$  with  $\text{Br}$ , remove  $\text{AgBr}$ , and precipitate  $\text{H}_2\text{SO}_4$  as usual ; or absorb in neutral  $\text{Cd}$  salt and titrate liberated acid with  $\text{KHO}$ . Later (lviii., 208) absorbs  $\text{H}_2\text{S}$  in  $\text{Hg}(\text{CN})_2$  and  $\text{AmCl}$ , so as to avoid washing the  $\text{AgBr}$ .
667. MORRELL (*C. N.*, xxviii., 229).—Pass evolved  $\text{H}_2\text{S}$  into ammoniacal  $\text{Cd}$  solution ; precipitated sulphide dried and weighed.



668. LUTSCHER (*J. I. S. I.*, 1888, i., 379).—Absorb  $\text{H}_2\text{S}$  in alkaline  $\text{PbO}$ , boil, and settle the  $\text{PbS}$  by whirling the graduated tube in a centrifugal machine. Accurate to 0.003 per cent.
669. SCHULTE (*C. N.*, lxxv., 47).—Pass  $\text{H}_2\text{S}$  through heated tube into  $\text{CdA}$ , add  $\text{CuSO}_4$ , filter off  $\text{CuS}$ , and ignite to  $\text{CuO}$ . Both P and As interfere if the solution is passed directly into Cu solutions (554).
670. CRAIG (*C. N.*, xlvi., 199 and 272).—Absorb in ammoniacal  $\text{H}_2\text{O}_2$ , acidify, and add  $\text{BaCl}_2$ . All the S is evolved as  $\text{H}_2\text{S}$ , even from cupriferos and white irons. (See 675 and 688.)
671. MEINECKE (*J. I. S. I.*, 1888, ii., 333).—As 670 ; in a current of H, and absorbs in  $\text{H}_2\text{O}_2 + \text{NaHO}$ .
672. REIS and WIGGERT (*J. I. S. I.*, 1891, ii., 325).—Evolve in current of  $\text{CO}_2$ , absorb in  $\text{AmHO} + \text{H}_2\text{O}_2$ , and precipitate with  $\text{Ba}(\text{NO}_3)_2$  from an exactly neutral solution. The precipitate is easily filtered.
673. REIS (*J. I. S. I.*, 1895, i., 509).—Use  $\text{HCl}$  of 1.09 sp. gr.; boil to thick fluid, and absorb  $\text{H}_2\text{S}$  in  $\text{AmHO} + \text{H}_2\text{O}_2$ .  $\text{H}_2\text{O}_2$  may contain  $\text{H}_2\text{SO}_4$  or fluo-silicic acid.  $\text{CO}_2$  must not be used to carry  $\text{H}_2\text{S}$  forward. By boiling  $\text{H}_2\text{O}_2$  solution, S may be oxidized beyond  $\text{H}_2\text{SO}_4$ , difficult to precipitate with  $\text{BaCl}_2$ . All these points are guarded against.
674. SPULLER and KAHLMANN (*J. I. S. I.*, 1895, i., 512).—Absorb in  $\text{Na}_2\text{O}_2$  in current of deoxidized air. Decompose  $\text{Na}_2\text{O}_2$  by boiling and  $\text{KMnO}_4$ . Precipitate as usual.
675. ROCHOLL (*C. N.*, xlvi., 236).—S may always be found in the residue, particularly when cupriferos irons are assayed.
676. BRUGMAN (*C. N.*, liv., 290).—Copper is no detriment to the evolution process, even when present up to 1 per cent.
677. BRAND (*J. I. S. I.*, 1884, 660).—Absorb in a burette of glass beads moistened with Br water ; precipitate as usual.
678. TROILIUS (*J. I. S. I.*, 1884, 333).—Absorb in  $\text{HCl} + \text{Br}$ , pour into  $\text{BaCl}_2$ , and boil to drive off Br.
679. BLUM (*J. I. S. I.*, 1892, ii., 515).—When  $\text{H}_2\text{S}$  is absorbed as in 678, subsequent evaporation is necessary, not because Br interferes with the formation of  $\text{BaSO}_4$ , but in order to destroy oily hydrocarbons.
680. ROLLET (*J. I. S. I.*, 1880, 359) and GONTHIERE (*J. S. C. I.*, 1896, 830).—The  $\text{HNO}_3$  and  $\text{BaSO}_4$  process is untrustworthy. Heat finely-divided metal, fuel, or slag in H (and  $\text{CO}_2$ ). Collect  $\text{H}_2\text{S}$  in  $\text{AgNO}_3$  and weigh as  $\text{Ag}_2\text{S}$  or Ag. (See 720.)
681. PHILLIPS (*J. S. C. I.*, 1896, 218).—The evolved  $\text{H}_2\text{S}$  is accompanied by organic sulphur compounds (methyl sulphide and mercaptan) not easily oxidized (see 692, etc.) ; pass through hot tube and absorb, in a capacious bottle, with  $\text{HCl} + \text{Br}$ . (See 563.)
682. TREADWELL (*C. N.*, lxiv., 217).—The insoluble sulphide is heated with Fe in  $\text{CO}_2$ , the resulting ferrous sulphide treated with  $\text{HCl}$ , and the  $\text{H}_2\text{S}$  absorbed in  $\text{H}_2\text{O}_2 + \text{AmHO}$ . (*J. C. S.*, lxii., 1375).—Insoluble sulphides are quantitatively converted to  $\text{H}_2\text{S}$  by treatment with Sn and  $\text{HCl}$  without sulphates being attacked.

683. REED (*C. N.*, lxxii., 299).—Simple apparatus for absorbing  $H_2S$  in a small volume of liquid. Apparatus for same purpose by BLUM (*J. C. S.*, lxii., 1376 ; *J. S. C. I.*, 1893, 1062), MEADE (*J. S. C. I.*, 1897, 934), and MACKENZIE (*J. S. C. I.*, 1893, 624).

*b. Volumetric Estimation :*

684. ELLIOT (*C. N.*, xxiii., 61 and 143).—Absorb in  $NaHO$ , and determine  $H_2S$  in the acidified solution by titrating with iodine. The insoluble residue contains traces of S existing as sulphate.

685. PAYNE (*C. N.*, lxvi., 286) and LAUDIS (*C. N.*, lxxv., 218).—As 684. The standard iodine is prepared by adding a known amount of  $KMnO_4$  to an acid solution of  $KI$ .

686. WILSON (*C. N.*, lxiv., 252).—The iodine is standardized by an actual sample containing a known amount of sulphur.

687. KOPPMAYER (*C. N.*, xxix., 134).—Pass evolved  $H_2S$  in a current of  $H$  into iodized  $KI$ , and titrate the excess of free  $I$  with hypo.

688. PETERS (*C. N.*, xxv., 11).—With white irons or steels all the S is not evolved as  $H_2S$  in 684, part remains with the residue. (See 717.)

689. HERTING (*C. N.*, lxxv., 109).—As MORRELL (667), but titrate the  $CdS$  with iodine. It is unnecessary to expel air from the evolution flask with  $H$  or  $CO_2$ .

690. TREADWELL (*J. I. S. I.*, 1893, i., 408) and CROBAUGH (*J. I. S. I.*, 1899, ii., 486).—Absorb in ammoniacal  $CdCl_2$ , acidify, and titrate with iodine.

690a. RIEMER (*J. I. S. I.*, 1900, i., 434).—As 690. Wiborgh's method (710) is unsatisfactory.

691. THILL (*C. N.*, lxxxi., 54).—Evolve  $H_2S$  into alkaline arsenite, pass acid vapours from evolution flask until  $As_2S_3$  is precipitated, and titrate a filtered fraction of the excess  $As_2O_3$  with iodine.

692. PROST (*J. I. S. I.*, 1889, i., 390).—Part of the S is present in cast-iron as an insoluble organic sulphur compound.

693. HERTING (*J. I. S. I.*, 1899, i., 484).—Resumé of gravimetric and volumetric processes.  $H_2S$  must be passed through a hot tube to decompose accompanying  $(CH_3)_2S$  compounds.

694. MOORE (*J. S. C. I.*, 1900, 72).—Results obtained by direct oxidation and evolution differ more on 'chilled shot samples' than on the ordinary metal.

695. CAMPREDON (*C. N.*, lxxii., 299 ; and *J. I. S. I.*, 1897, ii., 503).—Evolve  $H_2S$  through heated tube along with  $H$  and  $CO_2$  into  $Zn\overline{A}_2$ , and titrate  $ZnS$  with iodine. Time, fifteen to thirty minutes.

696. HOOPER (*C. N.*, lxxviii., 191).—Collect  $H_2S$  in  $NaHO$ , and titrate the alkaline solution with  $PbNO_3$ .

697. HATTENSAUR (*J. S. C. I.*, 1891, 797).—Evolution with  $HCl$  gives for Siemens metals results identical with those gotten by 564.

698. BOUCHER (*C. N.*, lxxv., 121).—Absorb in  $NaHO$ , add to  $Fe_2Cl_6$ , and titrate  $FeO$  formed. Insoluble sulphides are treated with iron under charcoal, and estimated as above.

699. CAMMERER (*J. C. S.*, lxii., 18 and 278) and HANNS (*J. C. S.*, lxxiv., ii., 461).—Most metallic sulphides react with  $\text{Fe}_2\text{Cl}_6$  after the manner of 698.
700. WEIL (*J. C. S.*, l., 918).—Pass  $\text{H}_2\text{S}$  from mineral sulphide into  $\text{AmHO}$  solution of Cu and titrate the excess Cu in aliquot filtrate with  $\text{SnCl}_2$ . The addition of Zn promotes the decomposition of the mineral.
701. FRIEDHEIM (*J. C. S.*, lii., 396, 618, and 998).—Process 700 is unreliable, because CuO goes down with the sulphide, and the latter tends to oxidize and re-dissolve. Weil subsequently absorbs in a mixture of  $\text{CuSO}_4$ , NaK tartrate, and  $\text{NaHO}$ .
702. POPE (*J. C. S.*, lxxii., 123).—S is estimated in  $\text{Ca}_2\text{C}$  by decomposing with  $\text{H}_2\text{O}$ , then adding  $\text{H}_2\text{SO}_4$ , and absorbing  $\text{H}_2\text{S}$  in  $\text{Pb}\overline{\text{A}}_2$ .
703. KLOBULOW (*C. N.*, liv., 325).—The presence of nascent H in the evolution flask converts  $\text{SO}_2$  into  $\text{H}_2\text{S}$ , and may convert  $\text{H}_2\text{SO}_4$ —or even S—thereto; therefore add Zn to the dissolving substance.
704. FRIEDMANN (*J. C. S.*, l., 739).—Process 703 is not generally applicable.
705. HERTING (*J. I. S. I.*, 1898, ii., 562).—To powdered blast-furnace slag add N/10 iodine, dilute HCl, and titrate unreduced I with hypo.
706. CRAIG (*C. N.*, lxiv., 266).—Sulphur exists in blast-furnace slags wholly as CaS, and may be determined as in 670, using purified coal-gas to sweep out, etc. Insoluble sulphides are heated with Zn dust;  $\text{H}_2\text{S}$  evolved and estimated as in 698.
707. EGGERTZ (*C. N.*, xviii., 15).—Evolved  $\text{H}_2\text{S}$  colours Ag-Cu plate, which is then compared with standards. The amount of S in iron diminishes with time, at least on the surface.
708. RINMANN (*J. I. S. I.*, 1886, 397 and 1022).—Process 707 can be applied only to grey pig-iron; with white irons the results are very low. Möller says the test is quite untrustworthy.
709. OSMOND (*C. N.*, lvii., 142).—Pass  $\text{H}_2\text{S}$  through a series of bulbs containing equal volumes of standard  $\text{AgNO}_3$ . No  $\text{H}_2\text{S}$  passes any bulb until all the Ag is precipitated.
710. WIBORGH (*C. N.*, liv., 158).—Pass  $\text{H}_2\text{S}$  through calico soaked in  $\text{Cd}(\text{NO}_3)_2$ , and compare colour with permanent standards made in the same way. Air must be driven from the flask prior to evolution of  $\text{H}_2\text{S}$ .
711. COHEN (*J. S. C. I.*, 1890, 16).—A simple form of apparatus for making Wiborgh's test.
712. MORGAN (*C. N.*, lvi., 83).—Absorb  $\text{H}_2\text{S}$  in dilute  $\text{Pb}\overline{\text{A}}_2$ , and compare colour with a series of standards.
713. ARNOLD and HARDY (*C. N.*, lviii., 41, 59, and 71).—Process 712 gives PbS as a precipitate. Evolve  $\text{H}_2\text{S}$  in the presence of nascent H, collect in  $\text{NaHO}$ , add acidified  $\text{Pb}\overline{\text{A}}_2$ , and compare tints. Or pass evolved  $\text{H}_2\text{S}$  through a series of  $\text{Pb}\overline{\text{A}}_2$  tubes, as in 709, and count the number in which PbS is precipitated. Cu does not interfere.

714. LUCAS (*J. I. S. I.*, 1898, ii., 559).—Evolve  $\text{H}_2\text{S}$  by  $\text{HCl} + \text{H}_2\text{SO}_4$  ( $\text{H}_2\text{SO}_4$  alone gives low results), pass through hot tube into alkaline  $\text{PbO}$ , and estimate colorimetrically.
715. FUNK (*J. C. S.*, lxx., ii., 274).—Dissolve the zinc in  $\text{HCl}$ , absorb  $\text{H}_2\text{S}$  in  $\text{AmHO} + \text{ZnSO}_4$ , add paramidodimethylaniline and  $\text{Fe}_2\text{Cl}_6$  to the acidified solution, and compare the colour (blue) with standard solutions. Can detect 0.0001 per cent. sulphur.
716. SCHINDLER (*J. I. S. I.*, 1893, i., 408).—The  $\text{HCl}$  used should be concentrated in order to evolve all the S as  $\text{H}_2\text{S}$ .
717. WILLIAMS (*J. I. S. I.*, 1893, i., 409).—Less S is left in the residue when hot instead of cold  $\text{HCl}$  is used. One  $\text{NaHO}$  tube will absorb all the  $\text{H}_2\text{S}$ .
718. KONINCK (*J. I. S. I.*, 1895, ii., 597).—Add  $\text{SnCl}_2$  or Sn to evolution flask along with the metal, to prevent oxidation of the  $\text{FeO}$ .
719. DONATH (*J. C. S.*, lxxiv., ii., 159).—An  $\text{HCl}$  solution of  $\text{SnCl}_2$  reduces  $\text{SO}_2$  to  $\text{H}_2\text{S}$ .
720. HOLLERT (*C. N.*, xlvi., 13).—Heat to redness in a current of oxygen mixed with H and  $\text{CO}_2$ ; collect evolved  $\text{H}_2\text{S}$  in  $\text{AgNO}_3$ .
721. OTEHA (*J. I. S. I.*, 1898, i., 540).—Powdered coke mixed with Zn or Al and treated with  $\text{HCl}$ ; S, evolved as  $\text{H}_2\text{S}$ , is estimated colorimetrically with  $\text{Cd}\bar{\text{A}}_2$ .

### III. Miscellaneous Items.

722. SCHLOSSBERGER (*C. N.*, iii., 192 and 204).— $\text{Am}_2\text{MoO}_4$  in  $\text{HCl}$  gives a blue colour with  $\text{H}_2\text{S}$  or a metallic sulphide.
723. PRICE (*C. N.*, viii., 285).—Any alkaline melt on the outside of a crucible readily absorbs S from a gas flame. The presence of Mn causes the fused salt to creep.
724. KONINGH (*J. C. S.*, lxxviii., ii., 184).—Sulphur may be oxidized to  $\text{H}_2\text{SO}_4$  by boiling with KHO and permanganate.
725. MAR (*C. N.*, lxiii., 256).—Free  $\text{HCl}$  is favourable to the precipitation of Ba with  $\text{H}_2\text{SO}_4$ , but it does not eliminate the contamination with alkaline salts, nor does dissolving in  $\text{H}_2\text{SO}_4$  and diluting entirely, but evaporation of  $\text{H}_2\text{SO}_4$  solution of  $\text{BaSO}_4$  to crystallization does.
726. BROWNING (*C. N.*, lxxviii., 264).— $\text{HNO}_3$  and aqua regia are favourable to the formation of  $\text{BaSO}_4$ , as in 725; the precipitate is more crystalline and is not prevented by citrate, etc.
727. JANNASCH (*J. C. S.*, lxxvi., ii., 60).—Se is separated from  $\text{H}_2\text{SO}_4$  by boiling with hydroxylamine hydrochloride; Se is precipitated.
728. CARNOT and GOUTAL (*J. C. S.*, lxxii., ii., 555).—S exists in iron in combination with Mn by preference. On treating with Cu solutions, the sulphur combining with the Cu is equivalent to the Mn present in the steel.
729. SCHEURER-KESTNER (*J. S. C. I.*, 1885, 281).—When  $\text{Fe}_2\text{O}_3$  and  $\text{CaSO}_4$ ,  $\text{MgSO}_4$ , or  $\text{PbSO}_4$  are heated together,  $\text{SO}_3$  is given off. Probably

ferric sulphate is first formed and then decomposed at a higher temperature (see JANNASCH, *J. S. C. I.*, 1889, 820); this does not occur with  $\text{BaSO}_4$ .

730. ANON (*C. N.*, xix., 215).—By heating coke at  $300^\circ$  in a current of air at 2 to 3 atmospheres, all the sulphur is eliminated as  $\text{SO}_2$ ; the calorific power of the coke is increased.

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## PHOSPHORUS.

An enormous number of papers have been written on the estimation of phosphorus. Those relating exclusively to the analysis of agricultural material, except when dealing with the chemistry of the process are not noticed. Amongst the papers dealing with metallurgical materials, there is so much repetition that a selection of those presenting new features, or a grouping together of papers on similar lines, was necessary in order to make this section of the compilation usable. The classification is:

### I. SEPARATIONS FROM OTHER ELEMENTS.

### II. GRAVIMETRIC ESTIMATIONS.

- a. Precipitating Finally with Mo.
- b. Precipitating Finally with Mg.
- c. Precipitating Finally in Various Ways.

### III. VOLUMETRIC ESTIMATIONS.

- a. Of the Molybdate Precipitate.
- b. In Various Ways.

### IV. MISCELLANEOUS.

#### I. Separations from other Elements.

##### *Iron and Aluminium:*

731. SCHULZE (*C. N.*, i., 49).—Add  $\text{Sb}_2\text{Cl}_5$  to neutralized solution, boil the precipitate with  $\text{NaHO}$ , filter off Sb, etc., and precipitate P in the filtrate with Mg.
732. GIRARD (*C. N.*, v., 281; vi., 99) and ANTONY and MONDOLFO (*J. C. S.*, lxxvi., ii., 330).—Dissolve in  $\text{HNO}_3$  along with Sn, dissolve  $\text{SnO}_2$  in aqua regia, add  $\text{Am}_2\text{S}$  to precipitate traces of Fe, etc., and add Mg to the filtrate. (See 938.)
733. KESSLER (*C. N.*, xxiii., 76).—Dissolve Fe in  $\text{HNO}_3$ , evaporate, reduce with  $\text{H}_2\text{S}$ , precipitate with ferro-cyanide, and add Mg to the filtrate. MOHR (*J. C. S.*, lii., 864).—Similarly. Titrate P with uranium solution.

734. CHANCEL (*C. N.*, i., 72).—Precipitate from nitric solution with  $\text{AgNO}_3$  and  $\text{Ag}_2\text{CO}_3$ ; collect  $\text{Ag}_3\text{PO}_4$ , remove Ag as chloride, and precipitate P with Mg.
735. LYTE (*C. N.*, iii., 131).—Pass  $\text{H}_2\text{S}$  to form  $\text{FeO}$ , and remove As, etc.; add  $\text{K}\bar{\text{A}}$  and  $\text{Pb}\bar{\text{A}}_2$ , decompose precipitate with  $\text{Aln}_2\text{S}$ , and P from filtrate with Mg. Specially suited to separating P from Al and Cr.
736. MAYER (*C. N.*, iv., 75).—Requisite proportions of reagents when P is precipitated from tartrate solutions in order to keep up tartrate of magnesia.
737. WARINGTON (*C. N.*, viii., 19).—Citric acid does not form insoluble Mg salts when used for holding up Fe and Al in  $\text{AmHO}$  solutions.
738. FLIGHT (*C. N.*, xxxi., 214).—Boil with hyposulphite. Fe and P in filtrate separated with  $\text{Am}_2\text{S}$ . Al and P in precipitate separated with  $\text{NaHO}$  and  $\text{BaCl}_2$ .
739. DEROME (*C. N.*, xl., 292).—Ignite with an excess  $\text{Na}_2\text{SO}_4$ , and precipitate  $\text{Na}_3\text{PO}_4$ , extracted with water, with Ur, Ag, or Mg.
740. Lime.—SMITH (*C. N.*, vii., 212).—In the presence of tartaric acid,  $\text{CaO}$  can be precipitated as oxalate quite free from P.
741. WILLIAMS (*C. N.*, xxi., 170).—As 732; but dissolves the Sn-P compound in  $\text{KHO}$ , adds  $\text{H}_2\text{S}$ , etc.
742.  $\text{SiO}_2$  and  $\text{WO}_3$ .—SKEY (*C. N.*, xvi., 187).—Both  $\text{SiO}_2$  and  $\text{WO}_3$  form insoluble compounds with  $\text{P}_2\text{O}_5$ , and on this account P estimations are frequently imperfect. (See also 288 and 289.)
743. Vanadium.—HOLVERSCHEIT (*J. C. S.*, lviii., 1343).—Add  $\text{SO}_2$  to form  $\text{V}_2\text{O}_4$ , expel excess, and precipitate P rapidly with Mo at  $60^\circ \text{C}$ .
744. Uranium.—REICHARDT (*C. N.*, xxviii., 315).—Dissolve in  $\text{Na}_2\text{CO}_3$  and precipitate P with Mg.
745. Selenium.—Same process as 727.

## II. Gravimetric Estimations.

### a. Precipitating Finally with Mo:

746. EGGERTZ (*C. N.*, ii., 227).—Precipitates from  $\text{HNO}_3$ - $\text{HCl}$  solution of iron. The precipitate more soluble in 1 per cent.  $\text{HNO}_3$  than in water; tartaric acid prevents the precipitation. (See 819.)
747. FRESSENIUS (*C. N.*, xii., 73).—The  $\text{PMo}^1$  is not interfered with by  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{Fe}_2\text{Cl}_6$ , or  $\text{Al}_2\text{Cl}_6$ ; it is by large amounts of  $\text{HCl}$ ,  $\text{AmCl}$ , or dilution. The mixture is kept at  $65^\circ$  for six hours.
748. PARRY (*C. N.*, xxv., 229) and MORGAN (*C. N.*, lxxxiii., 154).—To solution of the metal add  $\text{AmHO}$  to complete precipitation, re-dissolve in  $\text{HNO}_3$ , and heat with a neutral solution of  $\text{Am}_2\text{MoO}_4$ .

<sup>1</sup> Used throughout as a contraction for ammonium phosphomolybdate.

749. HOLTOFF (*C. N.*, xxxvi., 234).—P<sub>2</sub>Mo may be formed in the presence of HCl, but the temperature must be kept low. The precipitate is soluble in aqua regia, and MoO<sub>3</sub> is precipitated. The magnesia precipitate may contain Mo. The acetate-magnesia process gives low results.
750. DEANE (*C. N.*, liv., 174).—Usual process. The precipitate has a tendency to pass the filter when formed in very acid (nitric) solutions.
751. EGGERTZ (*C. N.*, xlii., 87).—Deals with criticisms *re* the formation of the precipitate, its composition, reagents, estimation, and comparison with the Mo-Mg process.
752. HUNDESHAGEN (*C. N.*, lx., 169, 177, etc.).—The yellow precipitate is always (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub> · 12MoO<sub>3</sub> when dried at 130—150° C. The influence of alkaline nitrates, concentration, temperature, and acidity. The formation of P<sub>2</sub>Mo from neutral solutions with HNO<sub>3</sub>. The dissociation of P<sub>2</sub>Mo with HNO<sub>3</sub>, and the limiting molecular proportions of its constituents for quantitative estimation. The solubility of P<sub>2</sub>Mo in various salts, acid, and water. P<sub>2</sub>O<sub>5</sub> or MoO<sub>3</sub> may be estimated by titrating one against the other. Volumetric processes depending—(1) on the saturation of P<sub>2</sub>Mo with NaHO, and (2) on precipitating with HNO<sub>3</sub> from neutral solutions are outlined.
753. CARNOT (*C. N.*, lxxvii., 101).—Preliminaries like 777; but the P<sub>2</sub>Mo is dissolved and re-precipitated under well-defined conditions.
754. HANAMANN (*J. S. C. I.*, 1895, 598).—The P is precipitated and filtered at ordinary temperatures in order to assure a constant composition. Wash from the paper and ignite as 775.
755. PARRY and MORGAN (*C. N.*, lxxvii., 161).—Dissolve in aqua regia and eliminate HCl. Any excess of nitric acid is corrected by AmHO after<sup>1</sup> the Am<sub>2</sub>MoO<sub>4</sub> has been added.
756. VILLIERS and BORG (*C. N.*, lxxvii., 313).—The precipitation should be effected below 15°. In the presence of Fe and Al, a pure precipitate is not obtained.
757. JOHNSON (*C. N.*, lxxx., 157).—Above 50° the P<sub>2</sub>Mo is contaminated with Fe, Al, and Mn. The citrate method gives good results only by compensatory errors.
758. TAUBER (*J. I. S. I.*, 1883, 313).—The influence of AmNO<sub>3</sub>. Mo in the Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub> precipitate can be eliminated at high temperatures.
759. HUSS (*J. C. S.*, i., 1073).—AmCl added to the Fe<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub> solution in order to form Fe<sub>2</sub>Cl<sub>6</sub> and AmNO<sub>3</sub>. VORWERK (*J. C. S.*, lii., 299).—The results are low on account of the undecomposed nitrated carbon compounds.
760. LUCAS (*J. C. S.*, lxxiv., ii., 482).—Chlorides prejudicial. Ratio of MoO<sub>3</sub> to Fe present should be 3 to 2, and temperature 80°.
761. HANDY and LÆFFLER (*J. I. S. I.*, 1894, i., 612).—P is not completely precipitated by five minutes' shaking at 25°. (See 791.)

<sup>1</sup> AmHO added after the Am<sub>2</sub>MoO<sub>4</sub> accelerates the formation of the P<sub>2</sub>Mo, but generally gives high results.—H. B.



762. PHILLIPS and CARNAHAN (*J. I. S. I.*, 1894, i., 612).—Use a stream of gas or air for accelerating the precipitation of the P.
763. SCHMÖGER (*J. C. S.*, lxxii., ii., 230).—P is completely precipitated by Mo in the presence of citric acid.
764. TAMM (*C. N.*, xlix., 208).—P may be imperfectly precipitated when organic acids due to combined carbon are not destroyed. Prescribes the best mode of decomposing the iron, etc. Ores must be fused in order to get all the P into solution.
765. WOOD (*C. N.*, lii., 279).—By dissolving Fe in  $\text{HNO}_3$  and at once adding Mo, exactly two-thirds of the P is precipitated. After boiling with  $\text{CrO}_3$ , all the P is precipitated,  $\text{SiO}_2$  need not be separated.
766. EGGERTZ (*J. S. C. I.*, 1884, 179).—By merely dissolving and adding Mo as above, three-fourths of the P is precipitated. Deficiency due to existence of P other than as orthophosphate.
767. SCHNEIDER (*J. I. S. I.*, 1893, i., 407).—The nitric acid solution is further oxidized in order to change all the P to orthophosphate, and not to destroy organic acids.  $\text{KMnO}_4$  is better than  $\text{CrO}_3$  or  $\text{H}_2\text{O}_2$ . The  $\text{MnO}_2$  should be re-dissolved by  $\text{FeSO}_4$  and not oxalic compounds.
768. HAMILTON (*J. S. C. I.*, 1891, 904).—Showing that incomplete precipitation from nitric acid solutions is not due to carbonaceous matter, but to incomplete oxidation of the P.
769. CHEEVER (*J. I. S. I.*, 1884, 715 ; and 1885, 364).—Oxidize the iron solution with  $\text{HNO}_3 + \text{KClO}_3$ , dissolve the  $\text{MnO}_2$  in  $\text{HCl}$ , eliminate chlorine, and precipitate with Mo as usual.
770. REIS (*J. I. S. I.*, 1887, ii., 365).—Oxidation with  $\text{CrO}_3$  causes Cr to be occasionally precipitated with the P. Oxidize with  $\text{KMnO}_4$ , destroy excess with  $\text{HCl}$ , and proceed as usual. Or add  $\text{SnCl}_2$  to the  $\text{HCl}$  solution of the yellow precipitate and titrate the excess with permanganate.
771. M'KENNA (*J. I. S. I.*, 1894, i., 612).—Oxidation of chilled iron solutions with  $\text{KMnO}_4$  gives lower results than evaporation to dryness.
772. IBBOTSON and BREARLEY (*C. N.*, lxxxii., 270).— $\text{SiO}_2$  removed by evaporation with acids contains some P (742). Dissolve ferro-silicon in  $\text{HNO}_3 + \text{HF}$ , and proceed as in 889.
773. FINKENER (*C. N.*, xxxix., 42 ; and xlvii., 94).—Precipitate from solutions containing large amounts of  $\text{AmNO}_3$ , wash with very acid 20 per cent.  $\text{AmNO}_3$ , dissolve from the paper, and expel  $\text{AmNO}_3$  by gentle ignition.
774. TROILIUS (*C. N.*, xliv., 299).—Dissolve in  $\text{HNO}_3 + \text{HCl}$ . Expel  $\text{HCl}$ .  $\text{PMo}$  dried at  $95-140^\circ$ , or may be ignited so gently as to get rid of the paper without loss of weight.
775. MEINECKE (*C. N.*, liii., 53).—Add Mo at  $50-60^\circ$ , and allow to settle in the cold. Ignite at  $400-500^\circ$ ; the paper separately. Residue contains 4.02 per cent.  $\text{P}_2\text{O}_5$ , or, more accurately (*J. I. S. I.*, 1896, i., 540) 3.95 per cent.  $\text{P}_2\text{O}_5$ .



776. VORWERK (*J. I. S. I.*, 1887, i., 465).—Oxidize nitric acid solution with  $\text{CrO}_3$ , and ignite P<sub>Mo</sub> as 775; ignited precipitate contains 1.754 per cent. P. Si does not interfere with the precipitation of the P. Digestion with  $\text{CrO}_3$  does not complete the oxidation of spiegels.
777. HANNAMAN (*C. N.*, lxxxiii., 12).—By operating in the cold, or in presence of much  $\text{HNO}_3$  and  $\text{AmNO}_3$  the precipitation of  $\text{SiO}_2$  with the P<sub>Mo</sub> is avoided.
778. FÖRSTER (*J. I. S. I.*, 1901, ii., 523).—In basic slags  $\text{SiO}_2$  is precipitated with P<sub>Mo</sub> only when temperature exceeds  $80^\circ$ .
779. ANON. (*C. N.*, lxii., 28).—Oxidize the nitro-sulphuric solution with  $\text{CrO}_3$ , and ignite P<sub>Mo</sub> as 775 to  $\text{P}_2\text{O}_5\text{Mo}_{24}\text{O}_{68}$ .
780. NEUMANN (*J. C. S.*, lxxiv., ii., 454) and SHERMAN and HYDE (*J. C. S.*, lxxviii., ii., 757).—The P<sub>Mo</sub> is ignited to  $\text{P}_2\text{O}_5 \cdot 24 \text{MoO}_3$  by placing the platinum crucible within a porcelain one well into a Bunsen flame.
781. CARNOT (*C. N.*, xlix., 216).—All the P (in rocks, etc.) is precipitated along with some  $\text{Al}_2\text{O}_3$  by boiling with hyposulphite and acetate. Ignite, dissolve in  $\text{HNO}_3$ , and add Mo.
782. LECHARTIER (*C. N.*, xlix., 224).—Digest (soil) with aqua regia, precipitate Fe, etc., with  $\text{CaO}$  emulsion, ignite, digest with  $\text{HNO}_3$ , and precipitate solution (containing only a little iron) with Mo.
783. ARNOLD (*C. N.*, xliii., 147, 186, etc.).— $\text{Fe}_2\text{Cl}_6$  and free  $\text{HCl}$  cause low results; in any case all the P is not precipitated unless part of the iron is removed. Recommends an acetate-Mo-Mg process.
784. MACKINTOSH (*C. N.*, liii., 223).—On treating iron with  $\text{HCl}$ , all the P is not liberated as gas. Boil with  $\text{SO}_2$ , mix residue and the absorbing solution, and make acetate-Mo estimation. (See 879.)
785. SMITH (*C. N.*, xlv., 195) and MACFARLANE and WILSON (*J. I. S. I.*, 1893, i., 406).—Acetate-Mo, acetate-Mg, and direct precipitation with Mo processes described.
786. PATTINSON and STEAD (*J. I. S. I.*, 1888, i., 181).—As, when present, may be removed by repeated evaporation with  $\text{FeO}$  in  $\text{HCl}$ , precipitation with  $\text{H}_2\text{S}$ , or adding Zn to form arsenic hydride.
787. BENEZAT (*J. I. S. I.*, 1895, i., 505).—Eliminate As by evaporating ferric solution with  $\text{HCl}$  and  $\text{Na}_2\text{SO}_3$ . 0.1 per cent. As does not interfere when the precipitation is made at  $45^\circ \text{C}$ . Compares results by direct weighing, ignition,  $\text{SnCl}_2$  colour test, and  $\text{KMnO}_4$  titration of the P<sub>Mo</sub>.
788. CAMPBELL (*J. I. S. I.*, 1891, i., 436).—Oxalic acid added to  $\text{HCl}$  solution of the ore reduces As to  $\text{As}_2\text{O}_3$ , and  $\text{HCl}$  evaporation eliminates it.
789. PATTINSON (*J. S. C. I.*, 1893, 119).—Reduce solution of ore with  $\text{Na}_2\text{S}_2\text{O}_3$ , precipitate As with  $\text{ZnS}$ , and P from the filtrate (as ferric phosphate) with  $\text{BaCO}_3$ . Finish as usual.
790. SCHNEIDER (*J. I. S. I.*, 1893, ii., 529).—As is precipitated with the P only when the solution is a nearly neutral one.
791. BABBITT (*J. I. S. I.*, 1895, i., 134).—As is precipitated with the P beyond  $25^\circ \text{C}$ . At that temperature five minutes' shaking precipitates all the P, but the P<sub>Mo</sub> is very finely divided. (See 761.)

792. SCHNEIDER (*J. I. S. I.*, 1897, ii., 497).—A careful investigation of the best conditions for precipitating P. As comes down at ordinary temperatures ; Mo in acid solutions is reduced by Zn to  $\text{Mo}_2\text{O}_3$ , but is readily re-oxidized by the air.
793. REIS (*J. I. S. I.*, 1889, i., 396).—The rapid methods of estimating P allow very little As to contaminate the precipitate.
794. RIDSDALE (*J. I. S. I.*, 1895, i., 124).—Influence of varying amounts of As on the precipitation of PMo.
795. CARNOT and GOUTAL (*J. C. S.*, lxxii., ii., 520).—Treatment of the iron with neutral cupric-potassic chloride leaves all the P in the residue ; As passes into solution.
796. JENNINGS (*J. I. S. I.*, 1888, ii., 331).—Decompose ore with HCl, reduce with  $\text{SO}_2$ , and boil to precipitate Ti. Fuse the residue, add soluble portion to main filtrate, precipitate P along with a little Fe, and add Mo to the solution thereof as usual.
797. BASKERVILLE (*J. I. S. I.*, 1893, ii., 538).—Fuse titaniferous iron ore with  $\text{Na}_2\text{CO}_3 + \text{KNO}_3$ , digest with water, add  $\text{Fe}_2\text{Cl}_6$  to filtrate, and proceed as above.
798. PATTINSON (*J. S. C. I.*, 1895, 443 and 1022).—Ti interferes with precipitation of P. Add alum to FeO solution, precipitate  $\text{AlPO}_4$ , fuse, remove soda titanate, and precipitate P as usual. Hogg finds that Ti retards, but does not prevent, the precipitation of any P.
799. TAMM (*J. I. S. I.*, 1887, ii., 365).—The P must be determined in the basic acetate of iron precipitated from the solution of the Fe-Mn alloy.
800. MEINECKE (*J. I. S. I.*, 1888, i., 378).—Manganese interferes in no way with the direct precipitation of P with Mo.
801. MERTZ (*J. I. S. I.*, 1891, ii., 324) and ZIMMERMANN (*J. S. C. I.*, 1893, 293).—The PMo is weighed in a specific gravity bottle ; its actual weight being deduced from its known specific gravity (3.252).
802. ZIEGLER (*C. N.*, lxxvi., 298).—The ferro-chromium is fused with  $\text{NaNO}_3 + \text{KHO}$ , dissolved in  $\text{HCl} + \text{HNO}_3$ , HCl eliminated, and P estimated as usual.
803. HEMPEL (*J. S. C. I.*, 1890, 111).—Phosphor-tin is decomposed in a current of Cl, and P precipitated with Mo.
804. WOODBRIDGE (*J. I. S. I.*, 1889, ii., 476).—P exists in ores chiefly as apatite, and therefore merely boiling with nitric acid and adding Mo to the filtrate serves to estimate it.
805. MIXER (*J. I. S. I.*, 1896, ii., 454 ; and 1897, ii., 509).—The P in the insoluble residue of an ore is estimated after the manner of 808.
806. LYCHENHEIM (*J. I. S. I.*, 1894, i., 620).—The P of coal is all in the ash, and can be completely extracted with HCl.
807. CAMPREDON (*C. N.*, lxxv., 8).—The ash of the fuels must be fused with  $\text{Na}_2\text{CO}_3$  ; treatment with HCl merely does not dissolve out all the P. Also CROBAUGH (*J. S. C. I.*, 1893, 1061).
808. NORRIS (*J. I. S. I.*, 1894, ii., 500).—Dissolve ash with  $\text{HCl} + \text{HF}$ , eliminate these with  $\text{HNO}_3$ , and precipitate with Mo.

809. CAMP (*C. N.*, lxxxiii., 8).—P in coke ash as Norris. Arsenical ores are treated as in 788.
810. GLADDING (*C. N.*, lxxvii., 32).—P<sub>2</sub>Mo of constant composition. Direct weighing on tared papers for large amounts; final washing with alcohol.
811. BRUNNEMANN (*C. N.*, lviii., 108).—Digest basic slag with mixture of acids, evaporate at 110° to remove SiO<sub>2</sub>, take up in HNO<sub>3</sub>, and precipitate with Mo.
812. LOGES (*J. I. S. I.*, 1887, ii., 371).—Digest basic slag with H<sub>2</sub>SO<sub>4</sub> in order not to attack phosphides, which have not the same agricultural value as phosphates. Also KOSMANN (*J. C. S.*, 1., 489).
813. KLEIN (*J. I. S. I.*, 1886, 401 and 1024).—Decompose slag with KNaCO<sub>3</sub> + KClO<sub>3</sub> eliminate SiO<sub>2</sub>, and add Mo. Boiling HCl does not attack iron phosphide.
814. SPULLER and KALMANN (*J. C. S.*, lxvi., ii., 29).—Formation of silicomolybdate is favoured by AmNO<sub>3</sub> (See 847 and 904). Oxidize HNO<sub>3</sub> solution with KMnO<sub>4</sub>, destroy excess with KNO<sub>2</sub>, and add Mo.
815. CRISPO (*J. I. S. I.*, 1892, i., 489).—The amount of P<sub>2</sub>Mo formed depends on the proportion of P<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub>, and N<sub>2</sub>O<sub>5</sub> present. The simpler forms of the method are unreliable.
816. SEYDA (*J. C. S.*, lxxx., ii., 689).—Precipitate in presence of citric acid, and below 20° if Fe is present. Ignite as in 775.
817. LIPOWITZ (*C. N.*, i., 264).—Adds tartaric acid in making up the Mo reagent, so that MoO<sub>3</sub> may not be precipitated by an acid, by diluting, or by boiling. (See 746 and 763.)
818. JUPTNER (*J. I. S. I.*, 1894, ii., 491).—As 763. As much as 60 grms. tartaric acid per litre may be used.
819. VEITCH (*J. C. S.*, lxx., ii., 543).—The use of tartaric acid is permissible, but not advantageous.

*b. Precipitating Finally with Magnesia:* (See also 749, 757, 758, and 938).

820. CHAMPION and PELLET (*C. N.*, xxxv., 115).—Weighing as Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub> is less suited for estimating small amounts than direct weighing of the P<sub>2</sub>Mo.
821. KERN (*C. N.*, xxxv., 1).—Dissolve in aqua regia rather than HNO<sub>3</sub>, in order to destroy organic matter, which otherwise interferes with the precipitation as P<sub>2</sub>Mo. Dissolve P<sub>2</sub>Mo in AmHO and add Mg.
822. STOECKMANN (*C. N.*, xxxvi., 275).—The evaporated solution of the spiegel is heated to destroy organic matter, P<sub>2</sub>Mo formed in HNO<sub>3</sub> solution at 30°, and P re-precipitated with Mg.
823. FRICKE (*J. I. S. I.*, 1881, 283).—Dissolve in HNO<sub>3</sub>, ignite dried residue to destroy C, and make Mo-Mg precipitation.
824. PARNELL (*C. N.*, xxiii., 145) and FOERSTER (*C. N.*, lxvii., 241).—If both solutions are heated before mixing, the Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub> is free from impurity. A correction for bulk of liquid is necessary. (See 838 and 844.)

825. OGILVIE (*C. N.*, xxv., 277).—0.3 grm.  $P_2O_5$  may be completely precipitated with Mo. Use 40  $MoO_3$  to 1  $P_2O_5$ . Precipitate finally with Mg.
826. GILBERT (*C. N.*, xxviii., 225).—Mg mixture should be made up without sulphate, otherwise MgO is precipitated. Uranic titration of  $P_2O_5$ .
827. ATKINSON (*C. N.*, xxxv., 127).—Silicates introduce positive errors into the Mo-Mg estimation.
828. AGTHE (*C. N.*, xlv., 284).—Complicated Mo-Mg process. The solution should be cooled to ordinary temperature before the PMo is filtered off.
829. STUNKEL (*C. N.*, xlvi., 66).—Form PMo in presence of 15 per cent.  $AmNO_3$ , dissolve in  $AmHO$ , and add Mg drop by drop (See 870). Filter after two hours' standing.
830. WEISSMANN (*J. I. S. I.*, 1890, i., 370).—Oxidize nitric acid solution with  $KMnO_4$ , reduce excess with  $H_2O_2$ , and precipitate as usual.
831. BAMBER (*J. I. S. I.*, 1894, i., 319).—Add  $Na_2CO_3$  to  $HNO_3$  solution of the iron short of alkalinity, leach evaporated residue with  $Na_2CO_3$ , and precipitate filtrate with Mg. All the As is precipitated also.
832. ROODE (*J. C. S.*, lxxviii., ii., 414).—The results are more exact when a known amount of  $Na_3PO_4$  is added and finally deducted.
833. RUNYAN and WILEY (*J. C. S.*, lxx., ii., 126).—The same remark (832) applies to the citrate process.
834. WDOWISZEWSKI (*J. I. S. I.*, 1897, ii., 502).—Mo-Mg process. Five minutes' shaking completes the Mg precipitation.
835. GLADDING (*C. N.*, xlvi., 213).—Precipitation with Mg in neutral, faintly alkaline, and strongly alkaline solutions; the addition of Mg mixture in drops, etc.
836. MYHLERTZ (*J. S. C. I.*, 1894, 67).—The turbidity sometimes seen on dissolving PMo in  $AmHO$  is due to ferric phosphate, and is prevented by dissolving in alkaline citrate solutions.
837. WAKEMANN (*J. C. S.*, liv., 1131).—The Mg precipitate may be washed with advantage by dilute  $AmHO$  containing alcohol.
838. GLADDING (*C. N.*, xlvii., 71).—The correction for solubility of Mg precipitate in mother-liquor and wash-water is practically nil.
839. SCHMÖGER (*J. C. S.*, lxxiv., ii., 455).—The Mg precipitate need not be ignited apart from the paper if that loosely adhering is shaken into the crucible.
840. PEITZCH, etc. (*C. N.*, xliii., 7).—Mg added gradually, and precipitate ignited strongly in order to volatilize any adherent  $MoO_3$ .
841. BROCKMANN (*C. N.*, xlvii., 84).—Dissolve the Mg precipitate with  $HNO_3$  into a weighed crucible, evaporate, and ignite.
842. NEUBAUER (*J. C. S.*, lxx., ii., 73).—The lid of the crucible is coated with MgO, in order to retain  $P_2O_5$ , which is volatilized on ignition. For a "decomposition formula" wherewith to correct results see MEINECKE, *J. I. S. I.*, 1896, i., 541. Chlorides do not interfere with the Mo precipitation.

843. LINDO (*C. N.*, xlviii., 217, 230, and 239).—Investigates precipitation with Mg, influence of heat, excess Mg, mode of adding Mg, concentration, alkalinity, solvent action of chlorides, oxalates, citrates, etc., etc.
844. LASNE (*C. N.*, lxxvi., 268).—Mg precipitation. Influence of time, mechanical shaking, dilution, and lime. Is the ignited precipitate  $\text{Mg}_2\text{P}_2\text{O}_7$ ? The presence of citric acid is necessary always. *C. N.*, lxxviii., 166.—The precipitate is completely insoluble in a solution containing one-third its volume of AmHO.
845. NEUBAUER (*J. I. S. I.*, 1892, ii., 513; and 1893, ii., 529).— $\text{P}_2\text{O}_5$  is lost on heating when the precipitate is formed in solutions containing too much ammonia.
846. NEUBAUER (*C. N.*, lxx., 213).—Influence of AmHO salts, excess Mg, and alkalinity on the composition of the precipitate. Ignite precipitate white at low temperature, then blast.
847. KENNEPOHL (*J. I. S. I.*, 1888, i., 385).—Basic slag contains but little Fe phosphide. Decompose with HCl and make Mo-Mg precipitations. Silico-molybdate is soluble in 3 per cent.  $\text{HNO}_3$ .
848. MULLER (*J. I. S. I.*, 1881, 708).—Blast-furnace slag is dissolved in HCl, evolved phosphoretted hydrogen oxidized with  $\text{HNO}_3$  and estimated as usual.
849. OLIVERI (*J. I. S. I.*, 1891, ii., 331).—Decompose basic slag with  $\text{HCl} + \text{KClO}_3$  and estimate with Mg as usual.
850. VOGEL (*J. C. S.*, liv., 991).—Decompose with HCl and precipitate with Mg from citrate solution.
851. REIS (*J. C. S.*, lvi., 439).—Summarizes the processes suggested for decomposing and estimating P in basic slags, and suggests modifications.
852. SHIMER (*C. N.*, lviii., 165).—Dissolve iron in  $\text{HNO}_3$ , add  $\text{KMnO}_4$ , destroy excess with HCl, evaporate with  $\text{H}_2\text{SO}_4$ , and precipitate with Mo and then Mg. Works well with titaniferous irons. Sulphates can entirely replace nitrates in the Mo precipitation.
853. MYHLENBERG and DROWN (*J. I. S. I.*, 1881, 657).—P can be completely precipitated from nitro-sulphuric filtrate of the silicon estimation (205) with  $\text{Am}_2\text{MoO}_4$ .
854. LINDO (*C. N.*, xlix., 247).—Comparison of methods,  $\text{SiO}_2$  should always be removed.
855. CETTEL (*J. C. S.*, lxxii., ii., 157).—Digest phosphor-bronze with  $\text{HNO}_3$ , fuse  $\text{SnO}_2$  with KCN, boil filtrate with HCl to eliminate HCN, and precipitate with Mg. As does not interfere.
856. WICKHORST (*J. C. S.*, lxxiv., ii., 46).—Dissolve phosphor-bronze, Cu-Sn alloys, etc., in aqua regia, add AmHO, pass  $\text{H}_2\text{S}$ , and add MgO to the filtrate.
857. BRUYN (*J. C. S.*, lxvi., ii., 217).—Decompose phosphor-tin with Br, evaporate with HCl, electro-deposit Sn, and precipitate P with Mg.
858. DUDLEY and PEASE (*J. S. C. I.*, 1894, 665).—Precipitation as ferric phosphate, and then as PMo. Dissolve in AmHO, pass  $\text{H}_2\text{S}$  to remove As and Mo, and precipitate evaporated filtrate with Mg.

859. ABEL (*C. N.*, vi., 133).—Precipitate basic phosphate of iron from FeO solution, dissolve in HCl, add AmHO and H<sub>2</sub>S, and precipitate filtrate with Mg.
860. SPILLER (*C. N.*, xiii., 170).—As 859 ; but precipitates the ferric phosphate along with a little ferrous carbonate by means of Am<sub>2</sub>CO<sub>3</sub>.
861. TOSH (*C. N.*, xvi., 168).—Mainly as 860. Precipitates the P with Mg in the presence of citric acid without separating the iron. NICKLES (*C. N.*, vii., 87).—Decompose Fe with Br, and, after adding AmHO, tartrate, and alcohol, precipitate with magnesia.
862. RILEY (*C. N.*, xxxvii., 68).—Dissolve in HCl, and form ferric phosphate as 859 ; but precipitate finally from an AmHO solution containing 13 grms. of citric acid. Results of Mo process are low.
863. CLYMER (*J. I. S. I.*, 1888, i., 378).—Reduce to FeO with bisulphite, precipitate ferric phosphate with acetate, and make citro-magnesian precipitation. Digest Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub> with HNO<sub>3</sub>, and deduct the residue from the first weighing.
864. SCHEIDING (*J. C. S.*, lxviii., ii., 291).—Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub> obtained from citrate solution should, if black, be re-heated with AmNO<sub>3</sub>.
865. PELLET (*J. C. S.*, lxxx., ii., 532).—Heat black precipitates with H<sub>2</sub>SO<sub>4</sub> and weigh as pyro-sulphomolybdate.
866. MEYER and SCHMIDT (*J. S. C.*, I., 1882, 372).—Perfect precipitation of the P takes place only when the citrate and AmHO are in the proportion of 1 to 2.
867. KNAP (*C. N.*, xv., 207).—In the presence of tartaric acid, P is not precipitated by Mg from an alkaline liquid if Al is also present.
868. GLASER (*C. N.*, li., 285).—Not more citrate is used than is necessary to keep all the Ca in solution. Process used for Fe ores. (*J. C. S.*, lxviii., ii., 138).—A large excess of Mg is necessary in order to form the ordinary triple phosphate.
869. REITMAIR (*J. C. S.*, lx., 243).—The use of citric acid always gives imperfect results however the process is modified. (See 757.)
870. LORENZ (*J. C. S.*, lxiv., ii., 185) and KILGORE (*J. C. S.*, lxviii., ii., 329).—In the absence of citric acid, MgO is always simultaneously precipitated, even when the mixture is added in drops.
871. TOLLENS (*C. N.*, xlv., 209).—Moisten Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub> with AgNO<sub>3</sub> and heat quickly ; a yellow colour indicates contamination by MgO, CaO, or their phosphates or citrates.
872. SHUTZER (*J. C. S.*, lvi., 186).—The complete precipitation from citrate solutions is assured by adding pulped filter-paper and stirring five minutes. SEYFERT (*ibid.*, 548) rubs a cropped feather against the beaker side with the same object.
873. OGILVIE (*C. N.*, xxi., 205).—When the solution of a mineral which has not been evaporated is precipitated from citrate solutions with Mg, Fe and Al go down as silicate.
874. OGILVIE (*C. N.*, xxxi., 274 ; and xxxii., 5, 12, and 70).—Investigates influence of AmHO and various salts, Fe and Al, and mixtures of these

on the Mg precipitation in hot and cold solutions. Condemns the process when Fe or Al is present.

875. PARNELL (*C. N.*, xxxii., 222).—Disputes conclusions of 874. The British Association Reports on means of estimating  $P_2O_5$  in "commercial products" (*C. N.*, xxxii., 172; and xxxviii., 63) refer to these points and summarize work on the citric acid, magnesian, uranic, and molybdic processes.
876. MULLER (*J. I. S. I.*, 1888, i., 386).—Solution of basic slag at once precipitated with citro-magnesian reagent, added in drops, before making alkaline with ammonia.
877. EDWARDS (*C. N.*, lxiv., 275), VON REIS (*C. N.*, lix., 107), and JOLLES (*C. N.*, lxvi., 262).—Each precipitate with Mg from citrate solutions after decomposing the slag with various acids.
878. KALMANN (*C. N.*, lv., 248).—Heat borings with CaO and  $KNaCO_3$ , digest with citric acid, and precipitate filtrate with Mg.
879. TANTIN (*C. N.*, xviii., 252).—Treat metal with HCl, pass gases through KHO into  $AgNO_3$ , decompose precipitate with aqua regia, and precipitate with Mg. (See 784.)
880. ADRIANZ (*C. N.*, xxvi., 60).—As 883; but reduce to FeO with hyposulphite, and precipitate finally with Mg. Al does not interfere.
881. LIEBRICH (*J. I. S. I.*, 1895, i., 504).—To HCl solution add  $Am_2S$ , evaporate filtrate after adding Mg, ignite, re-dissolve in HCl, add  $AmHO$ , and collect the precipitated ammonium magnesium phosphate.

*c. Precipitating Finally in various Ways:*

882. SUTTON (*C. N.*, i., 97 and 122).—Precipitate as phosphate of Ur and ammonia. Ca, Mg, and Ba do not interfere. Fe must be reduced to FeO.
883. CHANCEL (*C. N.*, i., 230; and iii., 3).—Acid nitrate of Bi precipitates either ortho-, pyro-, or metaphosphate from  $HNO_3$  solutions as  $Bi_2PO_4$ . Chlorides and sulphate interfere, and Fe must be reduced to FeO (with  $H_2S$ ) before precipitating the P.
884. PISANI (*C. N.*, iii., 211).—Precipitate as uranium phosphate from acetic solutions. Mg is perfectly separated. Fe and Al interfere.
885. BIRNBAUM (*C. N.*, xxii., 227).—Precipitate as 883, dissolve in HCl, add  $Am_2S$ , and estimate P in the filtrate with Ur.
886. MUNROE (*C. N.*, xxiv., 18 and 32).—To alkaline phosphate add  $Al_2(SO_4)_3 + HgCl_2 + NaHO$ ; increased weight of ignited precipitate over that due to  $Al_2O_3$  is  $P_2O_5$ . Or precipitate with  $HgNO_3$ ,  $Hg(NO_3)_2$ , and NaHO, and ignite with CuO to retain  $P_2O_3$ .
887. WARINGTON (*C. N.*, xii., 209).—Describes the precipitation of P as a compound of Fe, Pb, Sn, Hg, and Ur.
888. KISSEL (*C. N.*, xx., 168).—Compares Mg, Mo-Mg, Ur, basic Fe, and Ur (volumetric) processes for estimating P. KITCHEN (*C. N.*, xxvii., 199).—Contrasts the Mg and Ur processes.



889. IBBOTSON and BREARLEY (*C. N.*, lxxxii., 55).—The PMo formed rapidly from  $\text{HNO}_3$  solution is dissolved in AmHO, poured into excess HCl,  $\text{Pb}\bar{\text{A}}_2$  added, and, after heating, poured into a mixture of Am $\bar{\text{A}}$  and AmCl. The  $\text{PbMoO}_4 \times 0.007 = \text{P}$ .
890. IBBOTSON and BREARLEY (*C. N.*, lxxxiii., 122).—Particulars of 889 for pigs, Cr and As steels. Very rapid working; final estimation as  $\text{Pb}_3(\text{PO}_4)_2 \cdot 24\text{PbMoO}_4$ .

### III. Volumetric Estimations.

#### *a. Of the Molybdenum Precipitate:* (See also 770.)

891. MACAGNO (*C. N.*, xxxi., 197).—Reduce acid solution of the PMo with zinc to  $\text{Mo}_2\text{O}_3$ , and titrate with  $\text{KMnO}_4$ .
892. DROWN (*C. N.*, lx., 20).—Dissolve in 1.135  $\text{HNO}_3$  (see 206), oxidize to orthophosphate with  $\text{KMnO}_4$ , clear with tartaric, and titrate PMo as 891. Silico-molybdate is soluble in dilute  $\text{HNO}_3$ .  $\text{Mo}_2\text{O}_3$  is not easily oxidized. (See 792.)
893. JONES (*C. N.*, lxii., 220 and 231).—PMo washed with  $\text{Am}_2\text{SO}_4$ , reduced by filtering through Zn, and titrated with  $\text{KMnO}_2$ .
894. EMMERTON (*J. I. S. I.*, 1886, 1018).—As 891; but filters off the zinc.
895. REIS (*J. I. S. I.*, 1886, 390).—As 891; or Mo-Mg process. The PMo formed in the cold is  $\text{Am}_3\text{PO}_4 \cdot 10\text{MoO}_3$ ; at 80–90°, it is  $\text{Am}_3\text{PO}_4 \cdot 11\text{MoO}_3$ . (See 752.)
896. HERTING (*J. I. S. I.*, 1897, i., 568; 1898, i., 534).—As 891. Reviews other rapid processes. Better to pour the Fe into the Mo solution.
897. SCHNEIDER (*J. C. S.*, lxiv., ii., 392).—The ore is decomposed with  $\text{HCl} + \text{HF}$ , evaporated with  $\text{H}_2\text{SO}_4$ , and PMo reduced with Zn as 894.
898. BLAIR and WHITFIELD (*J. I. S. I.*, 1895, ii., 593).—Analyse the yellow precipitate. The solution is reduced by zinc to  $\text{Mo}_{24}\text{O}_{37}$ .
899. AUCHY (*J. C. S.*, lxxii., ii., 343).—Reduction to  $\text{Mo}_2\text{O}_3$  probably; but, after filtering, it is  $\text{Mo}_{12}\text{O}_{19}$ .
900. DUDLEY (*C. N.*, lxxvii., 195).—The reduced solution must pass into excess  $\text{KMnO}_4$  without being exposed to the air, otherwise  $\text{Mo}_2\text{O}_3$  is partly oxidized. Also NOYES and FROHMAN (*J. I. S. I.*, 1895, i., 505).
901. HUNDESHAGEN (*J. C. S.*, lxviii., ii., 85), KILGORE (*Ibid.*, 183), CHEEVER (*J. I. S. I.*, 1885, 737), DUDLEY and PEASE (*J. I. S. I.*, 1893, ii., 528).—Give accounts of the zinc reduction process.
902. DUDLEY, DOOLITTLE, etc. (*J. I. S. I.*, 1894, ii., 492).—In order to obtain accurate results by titrating the reduced Mo, fixed conditions must be rigidly adhered to.
903. THILO (*J. I. S. I.*, 1887, i., 475).—Large PMo precipitates are not completely dried at 100°. Dissolve in AmHO, and titrate the excess, using litmus as indicator. Also WDOWISZEWSKI (*J. I. S. I.*, 1892, i., 487).



904. ISBERT (*J. C. S.*, lii., 526 ; and liv., 194).—Process 903 does not give concordant results. Suggests a method based on determining the AmHO in the precipitate. LIABLE (*Ibid.*).—The percentage AmHO in PMo is variable. Silico-molybdate is soluble in water, but not in AmNO<sub>3</sub>.
905. HANDY (*C. N.*, lxvi., 324).—Rapid precipitation of the PMo, wash with KNO<sub>3</sub>, dissolve in NaHO, and titrate excess with HNO<sub>3</sub>; NaHO standardized by pure PMo; As does not interfere (*J. C. S.*, lxvi., ii., 365).—As is eliminated by re-precipitating the PMo. Also ROTHBERG (*J. I. S. I.*, 1892, ii., 513).
906. KLOCKENBERG (*J. I. S. I.*, 1901, 516).—As 905, but wash with Na<sub>2</sub>SO<sub>4</sub>.
907. PEMBERTON (*C. M.*, lxix., 286).—One molecule P<sub>2</sub>O<sub>5</sub> requires precisely 23 molecules Na<sub>2</sub>O when the PMo is being neutralized. Na<sub>2</sub>O solution freed from CO<sub>2</sub> by Ba(HO)<sub>2</sub>. Also DAY and BRYANT (*C. N.*, lxx., 3).
908. MAHON (*J. I. S. I.*, 1897, ii., 503 ; and 1898, ii., 557).—As 905. P precipitated by shaking fifteen seconds ; result in eight minutes.
909. OHLY (*C. N.*, lxxvi., 200).—As 905 ; or the volume of the precipitate is measured in a Gotz tube.
910. JUPTNER (*C. N.*, lxxii., 172).—Measures PMo in Gotz tube. As is precipitated above 40—45° C. BORMAN (*J. I. S. I.*, 1890, i., 369 ; and ANON. (*J. I. S. I.*, 1885, 738).—Also measures the PMo in a graduated tube.
911. WEDDING (*J. I. S. I.*, 1887, 466).—Precipitates PMo without oxidizing the organic matter when the carbon is low, and measures it in a tube.
912. REINHARDT (*J. I. S. I.*, 1891, ii., 324).—Personal errors figure largely when P is estimated by measuring PMo in a graduated tube.
913. PEMBERTON (*C. N.*, xlvi., 4).—Add aqueous Am<sub>2</sub>MoO<sub>4</sub> to HNO<sub>3</sub> solution of P<sub>2</sub>O<sub>5</sub>; the operation is at an end when no further PMo is formed ; precipitate of constant composition. Observes the interference of many impurities. Not suitable for irons.
914. CALDWELL (*C. N.*, xlviii., 61).—Apparatus for noting the end-reaction in 913.
915. GRETE (*C. N.*, lx., 310).—Similar to 913 ; but adds a solution of glue to the titrated liquid.
916. SCHINDLER (*C. N.*, lviii., 61).—Dissolve PMo in AmHO, precipitate with Mg, and titrate the Mo in the filtrate with PbA<sub>2</sub> and tannin as in 1379.
917. GALBRAITH (*J. I. S. I.*, 1890, i., 142).—A few decigrams of steel are dissolved in aqua regia, and the turbidity due to PMo compared with standards in order to trace the oxidation of the P in the “basic” steel bath. See also ALESSANDRIA (*C. N.*, lxxiv., 45).<sup>1</sup>

<sup>1</sup> In practice the P is determined by hammering a spoon test down to a fixed size and observing the fracture. In this way the P may be estimated to a few hundredths of 1 per cent. (See WINDSOR RICHARDS, *J. I. S. I.*, 1890, i., 150.)

918. CHEEVER (*J. I. S. I.*, 1885, 738) and OSMOND (*C. N.*, lvi., 160).—Dissolve PMo in NaHO, acidify with HCl, and add  $\text{SnCl}_2$ . The blue colour is proportional to the amount of P. (See 787.)
919. NAMIAS (*J. I. S. I.*, 1891, i., 435).—Wash PMo with AmCl, digest with  $\text{Na}_2\text{S}_2\text{O}_3$ , and compare blue colour with standards.
920. JOLLES and NEURATH (*J. S. C. I.*, 1898, 493).—Colour test based on estimation of AmHO in PMo by Nessler test is unreliable; yellow colour of the KPMo can be used. Fe and  $\text{SiO}_2$  interfere.
921. WOODMAN and CAYVAN (*C. N.*, lxxxiv., 69).—Critical study of the colorimetric estimation of  $\text{P}_2\text{O}_5$  (in waters).
922. PAGNAUL (*J. C. S.*, lxxviii., ii., 167).—Dissolve PMo in AmHO, add ferro-cyanile, acidify, and compare brown colour with standard.
923. FAIRBANKS (*J. C. S.*, lxxii., ii., 72).—The  $\text{MoO}_3$  of the PMo is estimated iodometrically as in 1381.

*b. Volumetric Estimation in Various Ways:*

924. JOHNSON and JENKINS (*C. N.*, xl., 39).—In the presence of Al or Fe add tartaric acid and Mg, and titrate the collected precipitate with standard acid. The precipitate is soluble in citrate solutions.
925. SCHLICKUM (*C. N.*, xlvii., 106), SEGALLE (*J. C. S.*, lxxviii., ii., 184), GLUCKMAN (*Ibid.*, 329), HEBEBRAND (*J. S. C. I.*, 1898, 607), and many others.—Add standard AmHO and  $\text{MgSO}_4$  to neutral solution of  $\text{P}_2\text{O}_5$ , and titrate the excess of AmHO in the filtrate.
926. BONGARTZ (*C. N.*, li., 123), EMMERLING (*J. C. S.*, l., 741), KELMANN and MEISSELS (*C. N.*, lxxii., 28), LITTMANN (*C. N.*, lxxx., 178), and others.—The titration of  $\text{P}_2\text{O}_5$  in the presence of Ca, Mg, Fe, Al, etc., is made by noting the KHO used between the yellow colour of the methyl-orange and the reddening of phenolphthalein.
927. LINOSSIER (*J. C. S.*, lvi., 308).—Precipitate with bismuth nitrate, decompose with  $\text{H}_2\text{S}$ , filter, and titrate  $\text{P}_2\text{O}_5$  with soda and Porrier's orange.
928. KRATSCHMER (*C. N.*, xlvii., 83).—Add  $\text{AgNO}_3$ , filter off  $\text{Ag}_3\text{PO}_4$ , and estimate the excess of Ag. This is Perrots' process.
929. WHITE (*C. N.*, lvii., 187).—To sulphuric solution add  $\text{AgNO}_3$  and  $\text{CaCO}_3$ , and titrate excess  $\text{AgNO}_3$  in the filtrate.
930. HOLLEMANN (*C. N.*, lxxi., 102) and CLARK (*J. S. C. I.*, 1888, 311).—As 928. The Ag in the filtrate or precipitate being estimated with KCNS.
931. SCHWARZ (*C. N.*, viii., 207).—To acetic solution add  $\text{PbA}_2$ , filter, and estimate excess of Pb with  $\text{K}_2\text{Cr}_2\text{O}_7$ . Ca and Mg do not interfere.
932. WAVELET (*J. C. S.*, lxiv., ii., 597).—Titrate with  $\text{Pb}(\text{NO}_3)_2$ , using KI as indicator.
933. LINDEMANN and MOTTEN (*J. C. S.*, lxx., ii., 388).— $\text{P}_2\text{O}_5$  is precipitated as ammonio-manganese phosphate; the Mn converted to  $\text{MnO}_2$  and estimated iodometrically.

934. CHRISTENSON (*J. C. S.*, lxxii., ii., 282).—From a mixture of  $\text{KBrO}_3$  and  $\text{KI}$ , phosphoric acid liberates  $\text{I}$ , which is estimated with thiosulphate.
935. DAVY (*C. N.*, i., 181).—To acetic solution of the  $\text{P}$  add ferric oxychloride, using gallic acid as spot indicator.  $\text{FePO}_4$  is precipitated.
936. SPICA (*J. C. S.*, lxii., 912 ; and lxiv., ii., 299).—Titrate neutral solution with iron alum, the amethyst colour with salicylic acid being used as indicator.
937. BURNARD (*C. N.*, xvii., 99).—Titrate with uranium nitrate. The delicacy of the ferro-cyanide indicator is increased by drying and then again moistening with water. (See 733 and 826.)
938. JOULIE (*C. N.*, xxvii., 228, etc.).—Titration with  $\text{Ur}$  with or without citro-magnesian precipitation, according as  $\text{Fe}$ ,  $\text{Al}$ , etc., are present or not. Process 732 is interfered with by  $\text{H}_2\text{SO}_4$ . Examines best conditions for  $\text{Mg}$  precipitation from citrate solutions. (*C. N.*, lii., 85).—Improved citro- $\text{Mg}$  precipitation. Reasons for avoiding estimation as  $\text{Mg}_2\text{P}_2\text{O}_7$ .  $\text{HF}$  and  $\text{HCl}$  interfere with  $\text{Mo}$  precipitation.
939. VILLE (*C. N.*, xxx., 200).—As 938. Particularizing the estimation in the presence of  $\text{Ca}$ ,  $\text{Al}$ , and  $\text{Fe}$ .
940. GUERIN (*C. N.*, xlv., 175).—The  $\text{Ur}$  solution should be standardized under such conditions as obtain in practice.  $\text{Am}\bar{\text{A}}$  to be avoided. Also MOHR (*C. N.*, xlv., 248).— $\text{Fe}$  separated with ferro-cyanide.
941. BROCKMANN and HASWELL (*C. N.*, xlvii., 177).—The value per c.c. of the  $\text{Ur}$  solution varies with the amount used.
942. MALLOT (*C. N.*, lxv., 52).—Separate from  $\text{Fe}$  with  $\text{Mo}$ ; titrate  $\text{Mg}$  precipitate with  $\text{Ur}$  in the presence of cochineal, which marks the end by forming a bluish-green colour.
943. SPENCER (*J. C. S.*, xlvi., 436).—Add  $\text{Ag}_2\text{CO}_3$  to faintly acid solution, dissolve  $\text{Ag}_3\text{PO}_4$  in  $\text{HNO}_3$ , add  $\text{NaCl}$ , and titrate  $\text{P}_2\text{O}_5$  with  $\text{Ur}$ .
944. FIRBY (*C. N.*, lxvi., 293).—The  $\text{Ur}$  volumetric process 938 is unreliable.

#### IV. Miscellaneous.

945. GRUNER (*C. N.*, xxi., 142).—Very small amounts of  $\text{P}$  are detected by acting on the metal with acid and observing the spectrum of the burning hydrogen.
946. ALLEN (*C. N.*, xxiv., 119).— $\text{P}$  and  $\text{As}$ , when precipitated with  $\text{Mg}$ , are distinguished by adding  $\text{AgNO}_3$  to the washed crystals. Acetic acid intensifies the reaction.
947. BLAIR (*C. N.*, lvi., 227).—Sketches the various methods proposed for estimating  $\text{P}$ , and states some precautions for making the "acetate" and "molybdate" estimations.
948. WALLER (*C. N.*, ix., 117 and 131).—Particulars of processes used by fifteen analysts on samples of pig-iron. "The Lundberg (Law) Case."

949. ARTH (*C. N.*, lxii., 155) and MARTINOTTI (*J. C. S.*, lx., 1397).—The results of highly phosphoric slags may be vitiated by the formation of a hydrated ferric phosphate when the HCl is being eliminated by  $\text{HNO}_3$ .
950. The following references relate to the state in which P exists in irons :—SCHNEIDER (*J. I. S. I.*, 1886, 913 ; and *J. S. C. I.*, 1888, 125), CHEEVER (*J. I. S. I.*, 1897, i., 401 and 467 ; and ii., 290), JUPTNER (*J. I. S. I.*, 1894, ii., 487 ; and 1897, i., 224), CAMPBELL and BABCOCK (*J. I. S. I.*, 1897, ii., 492), and STEAD (*C. N.*, lxxxii., 221, etc.; and *J. I. S. I.*, 1900, ii.).

## CHROMIUM.

The arrangement is :

- I. SEPARATION FROM OTHER ELEMENTS.
- II. GRAVIMETRIC ESTIMATION.
  - a. In which Cr is the Base of the Weighed Salt.
  - b.       "               "       Acid       "       "
- III. VOLUMETRIC ESTIMATION.
  - a. Titrating with Ferrous Salt.
  - b. Iodometrically.
  - c. Miscellaneous Processes.
- IV. MEANS OF CONVERTING TO  $\text{CrO}_3$ .
  - a. Dry Ways.
  - b. Wet Ways.
- V. DETECTION OF CHROMIUM.
- VI. MISCELLANEOUS NOTES.

### I. Separation from other Elements.

*Iron.* (See also 983, 1538, 1775.)

951. GIBBS (*C. N.*, xi., 101).—Oxidize to  $\text{CrO}_3$  and precipitate Fe with acetate or  $\text{AmHO}$ . Similar process for Al.
952. BAUBIGNY (*C. N.*, l., 18).—Ignited chromite oxidized with  $\text{HNO}_3$  +  $\text{KClO}_3$  and Fe and Al precipitated by a slight excess of bicarbonate. The  $\text{CrO}_3$  reduced with  $\text{H}_2\text{S}$  and precipitated as hydrate.
953. BREARLEY (*C. N.*, lxxvii., 49).—Separation from  $\text{CrO}_3$  with acetates or alkalis the more complete the greater excess there is used. Deficiency due to basic ferric chromates.  $\text{NaHO}$  the best precipitant.
954. KNORRE (*C. N.*, lix., 232).—Iron precipitated from HCl solutions with nitroso- $\beta$ -naphthol. The Cr in the filtrate cannot be completely precipitated with  $\text{AmHO}$ .

955. HESS and CAMPBELL (*C. N.*, lxxxi., 159).—Cr is precipitated quantitatively from solutions containing Fe, Ca, Mg, Mn, Co, and Ni by phenylhydrazine.
956. BOUSSINGAULT (*J. I. S. I.*, 1886, 828).—Fe and Cr cannot be separated by heating in HCl gas, because  $\text{Cr}_2\text{O}_3$  is thus volatilized (see 966). HAVENS and WAY (*J. S. C. I.*, 1899, 1157) say the separation can be made at 200—300° in a stream of HCl containing Cl.
957. VENATOR and ETIENNE (*J. C. S.*, lii., 532).—Decompose the mineral with NaHO, evaporate solution of the fusion, and leach  $\text{Na}_2\text{CrO}_4$  from the dried mass.
958. BAMBER (*J. I. S. I.*, 1894, i., 319).—Add  $\text{Na}_2\text{CO}_3$  short of alkalinity to the  $\text{HNO}_3$  solution of the iron, evaporate, ignite, and dissolve out  $\text{Na}_2\text{CrO}_4$  with water.
959. JANNASCH and CLOEDT (*J. C. S.*, lxx., ii., 222).—Mix with  $\text{H}_2\text{O}_2 + \text{AmHO}$ , and heat under pressure. The filtered  $\text{CrO}_3$  is reduced and precipitated with hydroxylamine chloride and ammonia.

*Aluminium:* (See also 951, 952.)

960. CARNOT (*C. N.*, xliv., 85).—The Al is precipitated from  $\text{CrO}_3$  solution with sodium phosphate and acetate.
961. BREARLEY (*C. N.*, lxxvii., 179).—Similar paper to 953.  $\text{Na}_2\text{CO}_3$  the best alkaline precipitant;  $\text{Na}_3\text{PO}_4$  available.
962. HUNT, CLAPP, and HANDY (*C. N.*, lxxv., 223).—Cr-Al alloys are boiled with KHO; residue fused with  $\text{KHSO}_4$ , converted to  $\text{CrO}_3$ , but finally precipitated with AmHO.

*Chromic Acid:*

963. STORER and ELLIOT (*C. N.*, vi., 121).—Precipitate  $\text{Cr}_2\text{O}_3$  from dilute acid solution with AmHO.
964. BREARLEY (*C. N.*, lxxvii., 217).—Preceding process inaccurate. Separate with NaHO or  $\text{Na}_3\text{PO}_4$ .

*Uranium:*

965. GIBBS (*C. N.*, xxviii., 63).—Oxidize to  $\text{CrO}_3$ , and precipitate Ur with NaHO, or the  $\text{CrO}_3$  may be precipitated with  $\text{HgNO}_3$  if no other precipitable non-volatile body is present.
966. DITTE (*C. N.*, xxxvi., 100).—The oxides of Fe, Cr, and Ur are heated in H and then in HCl to volatilize the Fe (see 956). Dissolve Ur from the residue with  $\text{HNO}_3$ .
967. FORMANEK (*J. C. S.*, liv., 531).—To precipitate the  $\text{CrO}_3$  with  $\text{HgNO}_3$ , (965) is inaccurate. Ditte's process is also unsatisfactory.

*Vanadium:*

968. CLASSEN (*J. I. S. I.*, 1887, i., 473).—Precipitate together as lead salts, eliminate Pb from HCl solution with  $\text{H}_2\text{S}$ , fuse evaporated filtrate with NaHO and S, and extract V with water.

969. VON KLECKI (*C. N.*, lxi., 54).—Precipitate V with uranic nitrate from an acetic solution.
970. *Copper*.—PRUD'HOMME (*C. N.*, xxv., 215).—From a mixture of the oxides of Cu and Cr the Cu is dissolved by NaHO, but both oxides are dissolved by AmHO. (See also 1587.)
971. *Phosphorus*.—GRANGER (*C. N.*, lxxv., 95).—Fuse with KHO, dissolve, acidify with HNO<sub>3</sub>, and precipitate with molybdate.
972. *Mercury*.—JANNASCH (*J. C. S.*, lxxvi. ii., 60).—Precipitate the Hg with hydroxylamine in the presence of oxalic acid.

## II. Gravimetric Estimation of Chromium.

*a. Where Cr is the Base of the Weighed Compound:* (See also 1005.)

973. OUDESLUYS (*C. N.*, v., 254).—Add Na<sub>2</sub>CO<sub>3</sub> + KNO<sub>3</sub> to the KHSO<sub>4</sub> fusion, precipitate Al<sub>2</sub>O<sub>3</sub> with Am<sub>2</sub>CO<sub>3</sub>, reduce, precipitate with AmHO, and ignite to Cr<sub>2</sub>O<sub>3</sub>.
974. GENTH (*C. N.*, vi., 31).—As above; but omit the KNO<sub>3</sub>, and precipitate Al<sub>2</sub>O<sub>3</sub>, etc., by boiling with excess AmNO<sub>3</sub>.
975. CLOUET (*C. N.*, xxiv., 304).—Fuse ore for six hours with Na<sub>2</sub>CO<sub>3</sub>, reduce CrO<sub>3</sub> with alcohol, and precipitate with AmHO.
976. TAMM (*C. N.*, xxiv., 305).—In general like 973; but the CrO<sub>3</sub> is reduced with HCl, and the nitrous oxide evolved. (See 1076.)
977. KERN (*C. N.*, xxxv., 67).—Precipitate Fe and Cr together with Am<sub>2</sub>S, ignite, fuse with K<sub>2</sub>CO<sub>3</sub> + KNO<sub>3</sub>, and precipitate reduced filtrate with AmHO.
978. WALLER and VULTE (*C. N.*, lxvi., 17).—Fuse with Dittmar's flux (1017), evaporate extract with AmNO<sub>3</sub>, re-dissolve, reduce, and precipitate with AmHO. A resumé of the means of opening up chromites.
979. ZIEGLER (*C. N.*, lxvi., 295).—Fuse Fe-Cr with KHO + KNO<sub>3</sub>, in silver crucible in smoky flame, pass CO<sub>2</sub>, separate associated elements, and precipitate with AmHO. Instructions for estimating P, etc., in ferro-chromium.
980. FRESSENIUS and BAYERLEIN (*C. N.*, lxxvii., 141).—Treat chromite with HCl; residue, with Na<sub>2</sub>O<sub>2</sub>. After various separations (Fe with Na<sub>2</sub>O<sub>2</sub>), reduce with H<sub>2</sub>O<sub>2</sub>, and precipitate with AmHO.
981. NAMIAS (*J. I. S. I.*, 1890, ii., 853).—Fuse FeCr with KHSO<sub>4</sub>, precipitate neutralized solution with MgO, ignite, re-fuse, and precipitate reduced solution with AmHO.
982. MORSE and DAY (*C. N.*, xlv., 43; and xlvii., 177).—Fuse powdered chromite with KHO in an iron crucible, separate Al<sub>2</sub>O<sub>3</sub> with AmHO, reduce, and precipitate with BaCO<sub>3</sub>.
983. DOHLER (*J. S. C. I.*, 1899, 1157).—Precipitate with BaCO<sub>3</sub> from FeO solution, fuse, separate SiO<sub>2</sub>, etc., and precipitate as usual. (See 1018.)
984. REINHARDT (*J. I. S. I.*, 1889, ii., 480).—Process based on the fact that Cr<sub>2</sub>O<sub>3</sub> is precipitated by ZnO, while ferrous and manganous salts remain in solution.

985. ZIEGLER (*J. I. S. I.*, 1890, i., 372).—Decompose chromeisen with bisulphate, and proceed as 984, using hypophosphite to reduce the iron.
986. KERN (*C. N.*, xxxv., 107).—Fuse ore with  $\text{KHSO}_4$ , dissolve in  $\text{HNO}_3$ , add  $(\text{NH}_4)\text{HS}$ , dissolve  $\text{Fe}_2\text{O}_3$  from the ignited precipitate, and weigh the  $\text{Cr}_2\text{O}_3$  residue.
987. JANNASCH and MAI (*J. C. S.*, lxiv., ii., 500).—In presence of hydroxylamine  $\text{Cr}_2\text{O}_3$  is thrown down by ammonia as a violet-red precipitate, more easily washed than the green one.
988. SOUCHAY (*C. N.*, xlvii., 248).— $\text{Cr}_2(\text{HO})_6$  precipitated with  $\text{AmHO}$  in glass vessels is always contaminated.
989. TREADWELL (*J. S. C. I.*, 1882, 339).—Cr may be precipitated in glass vessels by  $\text{AmHO}$  without error. The precipitate strongly retains fixed alkalis.
990. BLOXAM (*C. N.*, lii., 194).— $\text{Cr}_2(\text{HO})_6$  precipitated with  $\text{AmHO}$  carries down large amounts of  $\text{MgO}$ ; also some  $\text{SO}_3$ .
991. ARNOLD (*C. N.*, xlii., 285).—Criticism of the volumetric process (1009). Decompose steel with acids, fuse dried residue with  $\text{Na}_2\text{CO}_3 + \text{KNO}_3$ , reduce filtered  $\text{CrO}_3$ , and precipitate with  $\text{AmHO}$ .
992. HOGG (*J. S. C. I.*, 1891, 340).—Discusses process 1009. Proceeds as in 991. Oxidize ignited  $\text{Cr}_2\text{O}_3$  with  $\text{HNO}_3 + \text{KClO}_3$  to separate  $\text{SiO}_2$ , etc., and finally precipitate with  $\text{AmHO}$ . Percentage approximated by comparing colour of samples dissolved in  $\text{H}_2\text{SO}_4$ . Paper washed with Br or Cl and  $\text{AmHO}$  does not reduce  $\text{CrO}_3$ . (See 1089.)
993. CARNOT (*C. N.*, xlv., 243).—Precipitate with sodium acetate and phosphate from a slightly acid solution. The precipitate ignited and weighed.
994. ARNOLD and HARDY (*C. N.*, lvii., 153).— $\text{Cr}_2\text{O}_3$  obtained by 991 may contain P; it is better to precipitate the Cr as basic phosphate ( $3\text{Cr}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5$ ), which can be obtained of invariably the same composition.
995. FAKTOR (*J. C. S.*, lxxviii., ii., 691).—From  $\text{CrO}_3$  or  $\text{Cr}_2\text{O}_3$  solutions containing  $\text{CrO}_3$  all the Cr is precipitated by boiling with hypo.
- 995a. NORTON (*C. N.*, lxxxiv., 262).—Under pressure  $\text{Cr}_2(\text{HO})_6$  is rapidly and completely precipitated by hypo.
996. STOCK and MARSACIN (*J. S. C. I.*, 1901, 391).—Add  $\text{KI} + \text{KIO}_3$  and a small excess of hypo, filter hot, and ignite to  $\text{Cr}_2\text{O}_3$ . Fe similarly; Ca and Mg don't interfere.

*b. Where Cr is the Acid of the Weighed Compound:*

997. GIBBS (*C. N.*, xi., 101).—Oxidize to  $\text{CrO}_3$  with Cl or Br in acetate solution, and precipitate with Pb or Ba. Ca, Mg, Zn, Ni, Co, and Mn do not interfere. Precipitation with  $\text{HgNO}_3$  should be made in the cold. Ore decomposed with potassium fluoride.
998. GIBBS (*C. N.*, xxviii., 63).—Berzelius's method (precipitation with  $\text{HgNO}_3$ ) is best performed in hot solutions. See also KONINCK (*J. S. C. I.*, 1900, 470).

999. BAUBIGNY (*J. S. C. I.*, 1884, 457).—Precipitation as  $\text{Hg}_2\text{CrO}_4$  not advisable in presence of ammonium salts. Precipitates with  $\text{Am}_2\text{S}$ .
1000. SCHÖFFEL (*C. N.*, xli., 31).—Treat iron with copper solution, fuse residue, and precipitate with  $\text{HgNO}_3$ ; or remove  $\text{SiO}_2$  and precipitate with  $\text{AmS}_2$ . High Cr irons not decomposed by Cu solutions; after fusion, a process like 1036 is used.
1001. BOUSSINGAULT (*J. I. S. I.*, 1886, 807).—Fuse with  $\text{KHSO}_4$ , precipitate Fe and Cr with  $\text{AmHO}$ , fuse with  $\text{Na}_2\text{CO}_3 + \text{KNO}_3$ , and precipitate with  $\text{HgNO}_3$ .
1002. CLARK (*J. I. S. I.*, 1895, ii., 602).—Decompose ore with  $\text{KHSO}_4$ , oxidize with  $\text{HNO}_3 + \text{KClO}_3$ , separate Fe and Al with  $\text{AmHO}$ , and precipitate as  $\text{PbCrO}_4$ .

### III. Volumetric Estimation of Chromium.

#### *a. With Ferrous Salts :*

1003. BRITTON (*C. N.*, xxi., 266).—Ignite ore with  $\text{KClO}_3$  and soda-lime, dissolve in dilute  $\text{HCl}$ , and titrate with  $\text{FeSO}_4$  and  $\text{KMnO}_4$ .
1004. CLARK (*C. N.*, xxiv., 286).—Ignite ore with  $\text{NaHO} + \text{MgO}$ , and titrate sulphuric solution with  $\text{FeSO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ .
1005. CLARK (*J. S. C. I.*, 1893, 340).—Dissolve steel in  $\text{HCl}$ , precipitate Cr with  $\text{Na}_3\text{PO}_4$  and  $\text{Na}_2\text{SO}_3$ , oxidize ignited precipitate with  $\text{MgO}$  and  $\text{NaHO}$ . Chromic oxide may also be precipitated as basic sulphite and, if pure, ignited to  $\text{Cr}_2\text{O}_3$ .
1006. SCHWARZ (*C. N.*, xlix., 201).—The  $\text{CrO}_3$  formed by alkaline fusion is added to excess  $\text{FeSO}_4$ , and titrated with  $\text{KMnO}_4$ . Pouring  $\text{FeSO}_4$  into  $\text{K}_2\text{CrO}_4$  may cause error through formation of chromic chromate.
1007. M'KENNA (*C. N.*, lxxx., ii., 67).—Dissolve in  $\text{HCl}$ , replace  $\text{HCl}$  with  $\text{HNO}_3$ , add  $\text{KClO}_3$ , boil to decompose it, and titrate  $\text{CrO}_3$  with permanganate. POWALLECK (*C. N.*, li., 83) also oxidizes and titrates in this way. (See also 470.)
1008. MAHON (*J. S. C. I.*, 1900, 72).—Oxidize  $\text{HNO}_3$  solution with  $\text{KClO}_3$ , add  $\text{AmHO}$  and titrate filtrate with  $\text{FeSO}_4$  and  $\text{KMnO}_4$ .
1009. GALBRAITH (*C. N.*, xxxv., 151).—Dissolve steel in dilute  $\text{H}_2\text{SO}_4$ , oxidize with  $\text{KMnO}_4$ , and titrate filtered solution with  $\text{FeSO}_4$ , etc.
1010. PETERSON (*C. N.*, l., 210).—As 1009; add  $\text{KMnO}_4$  to the  $\text{H}_2\text{SO}_4$  solution until  $\text{MnO}_2$  is plentifully formed.
1011. VIGNAL (*C. N.*, liii., 195).—A good account of the process depending on oxidation with permanganate. Dissolve iron by preference in  $\text{HNO}_3$ . The formation of  $\text{MnO}_2$  roughly indicates the amount of Cr present.
1012. ARNOLD (*C. N.*, lxxi., 292).—In strong  $\text{H}_2\text{SO}_4$  solutions, oxidation to  $\text{CrO}_3$  with permanganate is impossible.
1013. GALBRAITH (*J. I. S. I.*, 1893, i., 146).—Presence of Fe favours accuracy of process 1009. Modifies process by adding  $\text{NaHO}$ , filtering off  $\text{MnO}_2$ ,  $\text{Fe}_2(\text{HO})_6$ , etc., and titrating the filtrate.



1014. BARBA (*J. I. S. I.*, 1893, ii., 536).—Condemns process 1013. Dissolve in  $\text{HNO}_3$ , oxidize, precipitate Mn, Fe, etc., with  $\text{AmHO}$ , but re-dissolve the Fe in  $\text{H}_2\text{SO}_4$ , and titrate the filtrate.
1015. BREARLEY (*C. N.*, lxxvii., 131, 187, and 216).—Manganous salts precipitated with  $\text{NaHO}$  in presence of  $\text{CrO}_3$  partly reduce it. Process 1013 subject to error on this account.
1016. WAHLBERG (*J. I. S. I.*, 1889, i., 398).—Dissolve in  $\text{HNO}_3$ , ignite dried residue with  $\text{Na}_2\text{CO}_3$ ,  $\text{KClO}_3$ , and  $\text{MgO}$ , and titrate the filtered  $\text{CrO}_3$ .
1017. DITTMAR (*Quant. Chem. Anal.* p. 128).—Fuse chromite with borax-glass +  $\text{NaKCO}_3$ , and titrate the acidified extract. Instructions for complete analysis of ore. Also FIEBER (*J. C. S.*, lxxviii., ii., 512) and MACIVOR (*C. N.*, lxxxii., 97).
1018. STEAD (*J. I. S. I.*, 1893, i., 135).—Examination of 1009. Avoid filtration of  $\text{MnO}_2$  by dissolving in  $\text{HCl}$  and boiling off  $\text{Cl}$ . Or precipitate from ferrous solution as phosphate, ignite with  $\text{NaKCO}_3 + \text{MgO}$ , and titrate  $\text{CrO}_3$ .  $\text{BaCO}_3$  does not precipitate  $\text{Cr}_2\text{O}_3$  completely from ferrous solutions. Precautions against V. Chromeisen also oxidized by the above (tribasic) reagent, and extract titrated. Distribution of Cr in British irons.
1019. LEFFLER (*C. N.*, lxxvii., 156).— $\text{MnO}_2$  is soluble in strong  $\text{H}_2\text{SO}_4$ . Such a solution can oxidize  $\text{FeSO}_4$ , and may lead to error in processes like 1009.
1020. IBBOTSON and BREARLEY (*C. N.*, lxxxii., 209).—Decompose Fe-W-Cr alloys with  $\text{HF} + \text{HNO}_3$ , evaporate with  $\text{H}_2\text{SO}_4$ , and apply 1018.
1021. J. T. (*C. N.*, lxxix., 158).—When chromeisen is oxidized in the dry way and the frit dissolved in acid, some very fine portions of the alloy, having escaped oxidation, will exert a reducing action on the  $\text{CrO}_3$ .
1022. SCHNEIDER (*J. I. S. I.*, 1892, ii., 515).—Oxidize nitro-sulphuric acid solution of the steel with  $\text{PbO}_2$ ; decompose any permanganate formed by making alkaline and boiling. Titrate with  $\text{FeSO}_4$ .
1023. HARVEY (*C. N.*, xlvii., 86).—Heat  $\text{CrO}_3$  compound with  $\text{HCl} + \text{SnCl}_2$ , add  $\text{Fe}_2\text{Cl}_6$ , and determine  $\text{FeO}$  with  $\text{K}_2\text{Cr}_2\text{O}_7$ .
1024. SCHNEIDER (*J. I. S. I.*, 1886, 399).—Dissolve chromeisen in  $\text{H}_2\text{SO}_4$ , oxidize solution of dried residue with  $\text{Br}$ , precipitate Fe with  $\text{AmHO}$ , and titrate the filtrate.
1025. SPÜLLER and KALMANN (*J. I. S. I.*, 1893, ii., 537).—Fuse chromeisen with sodium peroxide, decompose excess by passing  $\text{CO}_2$ , and titrate the acidulated filtrate.
1026. SPÜLLER and BRENNER (*J. I. S. I.*, 1897, i., 570).—Modified process for FeCr. Acid solution of steel dried, fused as FeCr, and  $\text{CrO}_3$  estimated iodometrically.
1027. SANITER (*J. I. S. I.*, 1895, ii., 153).—Fuse FeCr with mixture of Na and Ba peroxides, and boil acidified solution with permanganate according to Stead's modification (1018) of 1009.

1028. RIDEAL and ROSENBLUM (*J. S. C. I.*, 1895, 1017).—Severe criticism of 1027. Ni from fusion crucible interferes with the ferro-cyanide indicator. Mn, Ni, and Fe separated before titration. The uses of  $\text{Na}_2\text{O}_2$  in chrome-iron and steel analysis.
1029. SANITER (*J. S. C. I.*, 1896, 155).—Discusses the criticisms of 1028.
1030. CARNOT and GOUTAL (*J. C. S.*, lxxii., ii., 521).—Treat with Cu solution (1000), fuse residue with  $\text{Na}_2\text{O}_2$ , and titrate  $\text{CrO}_3$ .
1031. KOSMANN (*J. I. S. I.*, 1889, ii., 479).—Oxidize the Fe solution with alkaline  $\text{H}_2\text{O}_2$ , and titrate a filtered fraction with  $\text{FeSO}_4$ .

*b. Iodometric Estimation of Chromium:*

1032. WALLER (*J. S. C. I.*, 1896, 436).—Decompose ore with  $\text{Na}_2\text{O}_2$ , and titrate  $\text{CrO}_3$  with  $\text{Na}_2\text{S}_2\text{O}_3$  and KI.
1033. O'NEILL (*C. N.*, v., 199).—Fuse ore with  $\text{KHSO}_4$ , precipitate with  $\text{Na}_2\text{CO}_3$ , fuse with  $\text{Na}_2\text{CO}_3 + \text{KClO}_3$ , and titrate  $\text{CrO}_3$  with  $\text{Na}_2\text{S}_2\text{O}_3$ , using KI and starch as spot indicator.
1034. ZULKOWSKI (*C. N.*, xix., 238).—Add KI to an HCl solution of  $\text{CrO}_3$ , and titrate liberated I.
1035. SEUBERT (*J. S. C. I.*, 1901, 69).—The titration may be at once proceeded with if the molecular ratios  $\text{K}_2\text{Cr}_2\text{O}_7 : \text{KI} : \text{H}_2\text{SO}_4 = 1 : 18 : 110$  are adopted.
1036. SELL (*C. N.*, xxxix., 131).—Fuse chromite with bisulphate and sodium fluoride, oxidize with  $\text{KMnO}_4$ , add  $\text{Na}_2\text{CO}_3$  and alcohol, and estimate  $\text{CrO}_3$  with KI.
1037. SELL (*C. N.*, liv., 299).—Oxidize with  $\text{H}_2\text{O}_2$  in alkaline solution, and titrate  $\text{CrO}_3$ . Al and Zn are without influence; Fe (filtered off) causes low results.
1038. BROWNING (*J. C. S.*, lxxii., ii., 73).—Add excess  $\text{As}_2\text{O}_3$  and  $\text{NaHCO}_3$  to  $\text{CrO}_3$  solution, and titrate with I. Ferric salts may be present. Also NAMIAS (*J. C. S.*, lxii., 1374) and BIALOBRZESKI (*J. C. S.*, lxxiv., ii., 184).—In like manner in the presence of acetates and acetic acid. Also REICHARD (*J. S. C. I.*, 1900, 854).
1039. DONATH (*J. I. S. I.*, 1894, ii., 493).—Pour ferric solution into alkaline permanganate, and estimate the iodine liberated by the  $\text{CrO}_3$ .  $\text{FeSO}_4$  not suitable for estimating small amounts of chromic acid.

*c. Miscellaneous Volumetric Processes:*

1040. DAVY (*C. N.*, iii., 274) and RUBE (*C. N.*, xii., 82).—Titrate acid solution of  $\text{CrO}_3$  with ferro-cyanide, using  $\text{Fe}_2\text{Cl}_6$  spot indicator.
1041. DONATH (*C. N.*, xliii., 253).—The neutral  $\text{Cr}_2\text{O}_3$  solution is run into hot alkaline standard  $\text{KMnO}_4$  until a yellow colour is obtained. Fe and Al do not interfere; Mn does. (See 416.)
1042. GIORGIS (*J. C. S.*, lxiv., ii., 554).—Oxidize alkaline ferric solution with  $\text{KMnO}_4$ , destroy excess with  $\text{H}_2\text{O}_2$ , reduce filtered  $\text{CrO}_3$ , and run into  $\text{KMnO}_4$  as in 1041.

1043. GIORGIS (*J. C. S.*, lxxii., ii., 350).—Add standard  $\text{KMnO}_4$  to  $\text{Cr}_2\text{O}_3$  solution, boil, and titrate excess  $\text{KMnO}_4$  with  $\text{N}/20 \text{Cr}_2(\text{SO}_4)_3$  solution.
1044. CARNOT (*J. I. S. I.*, 1889, i., 399) and PERRAULT (*J. I. S. I.*, 1893, i., 413).—Oxidize to  $\text{CrO}_3$  with  $\text{AmHO} + \text{H}_2\text{O}_2$ , boil off excess, and titrate with  $\text{H}_2\text{O}_2$  in acid solution.
1045. BERTHELOT (*J. C. S.*, lvi., 350 and 488).—The  $\text{H}_2\text{O}_2 + \text{CrO}_3$  reaction varies with the mode of admixture, temperature, and concentration.
1046. JEAN and PELLET (*C. N.*, xxxv., 213).—Decompose ore by fusion. To  $\text{CrO}_3$  add baryta-water and  $\text{CO}_2$  to precipitate excess thereof. The free alkali equivalent to the  $\text{CrO}_3$  is titrated with  $\text{H}_2\text{SO}_4$ .
1047. RUOSS (*J. C. S.*, lxxiv., ii., 644).—Add lead salt to  $\text{CrO}_3$  solution, and estimate the excess in a fraction of the filtrate.
1048. SOLTSEIN (*J. C. S.*, lx., 118).— $\text{CrO}_3$  titrated with  $\text{BaCl}_2$ , using hæmatoxylin or logwood indicator.
1049. PURGOTTI (*J. C. S.*, lxxii., ii., 349).—Acidified hydrazine sulphate acts quantitatively with  $\text{K}_2\text{Cr}_2\text{O}_7$ , liberating N. The N is measured at normal temperature and pressure. Similar process for Cu.
1050. BAUMANN (*C. N.*, lxvi., 181, etc.).—In acid solutions,  $\text{H}_2\text{O}_2$  oxidizes  $\text{CrO}_3$  to perchromic acid and then reduces it to  $\text{Cr}_2\text{O}_3$ . Liberated O gasometrically estimated.  $\text{CrO}_3$  formed by  $\text{H}_2\text{O}_2$  in alkaline liquids. These facts applied extensively to quantitative analysis.
1051. HILLEBRAND (*C. N.*, lxxviii., 227).—Traces of Cr in rocks, ores, etc., estimated by comparing as mono-chromate with standard solutions.
1052. NEUMANN (*J. C. S.*, lxviii., ii., 64).—By titrating neutral  $\text{Cr}_2\text{O}_3$  solution with sodium sulphide.

#### IV. Means of Converting to Chromic Acid.

##### a. In the Dry Way:

1053. CLARKE (*C. N.*, xvii., 232).—Chromite (and other refractory materials) is fused with sodium fluoride and bisulphate, and oxidized with hypochlorite; or at once by including  $\text{KNO}_3$  in the fusion.  $\text{CrO}_3$  not completely separated from Fe and Al by  $\text{Na}_2\text{CO}_3$ .
1054. NAMIAS (*J. S. C. I.*, 1891, 486).—Fuse ore with  $\text{KHSO}_4$ , precipitate water extract with  $\text{MgO}$ , and fuse with  $\text{KClO}_3 + \text{NaKCO}_3$ .
1055. MOISSAN (*C. N.*, lxvii., 137).—Powdered chromeisen is converted to  $\text{CrO}_3$  by melting with  $\text{KNO}_3$ .
1056. KAYSER (*C. N.*, xxxvi., 153).—Heat chrome-iron with a mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{CaO}$ .
1057. PEMBERTON (*C. N.*, lxiii., 241).—Chromite and  $\text{Na}_2\text{CO}_3$  are heated over night by a Bunsen, and next morning over the blast. Decomposition is complete.
1058. HAUSSERMANN (*J. S. C. I.*, 1892, 182).—Fuse powdered ore with  $\text{K}_2\text{CO}_3$  and  $\text{NaHO}$ .
1059. MASSIGNON and VATEL (*C. N.*, lxiii., 273).—Heat ore mixed with  $\text{CaCl}_2$  and  $\text{CaO}$  (or  $\text{CaCO}_3$ ).

1060. CLARK (*J. S. C. I.*, 1892, 501).—Ferro-chromium is not completely dissolved by  $\text{H}_2\text{SO}_4$  (1085). Oxidize with  $\text{MgO}$  or  $\text{CaO} + \text{NaHO}$ .  $\text{FeCr}$  is decomposed by heating with  $\text{Ca}(\text{HO})_2$ , or in the vapour of  $\text{S}$  or  $\text{CS}_2$ . Latter process available for steels.
1061. DONATH (*J. I. S. I.*, 1887, ii., 371).—Heat with barium peroxide, and extract  $\text{CrO}_3$  with acidulated water.
1062. KENNICUT and PATTERSON (*J. C. S.*, lx., 366).—Fuse with barium peroxide and  $\text{Na}_2\text{CO}_3$ , dissolve in  $\text{HCl}$ , re-oxidize with alkaline  $\text{H}_2\text{O}_2$ , acidify, and titrate.
1063. CLARK (*J. C. S.*, lxiii., 1081).— $\text{FeCr}$  and chromite are completely decomposed by  $\text{Na}_2\text{O}_2$ . Heat to make pasty, not to liquefy.  $\text{Na}_2\text{O}_2$  does not separate  $\text{Fe}$  and  $\text{Cr}$ .
1064. REINHARDT (*J. I. S. I.*, 1890, i., 375).—Fuse with soda-lime and  $\text{KClO}_2$ . Titrate with  $\text{FeSO}_4$ .
1065. SMITH (*C. N.*, lxiv., 44 and 218).—An electric current passed through molten potash containing chromiferous material completely oxidizes it to  $\text{CrO}_3$ . Titrate with  $\text{FeSO}_4$ .

*b. Conversion to  $\text{CrO}_3$  in the Wet Way:*

1066. STORER (*C. N.*, xxi., 198).—Strongly ignited  $\text{Cr}_2\text{O}_3$  and chromite are converted to  $\text{CrO}_3$  by boiling with  $\text{HNO}_3 + \text{HClO}_3$ . Precipitated as  $\text{BaCrO}_4$ .
1067. STODDART (*C. N.*, xxiii., 284).—Storer's process does not completely decompose chromite.
1068. PHILLIPS (*C. N.*, xxix., 28).—Decompose chromeisen with  $\text{H}_2\text{SO}_4$  in closed tubes, oxidize with  $\text{Na}_2\text{CO}_3$  and  $\text{Br}$ .  $\text{Zn}$ ,  $\text{Mn}$ ,  $\text{Fe}$ , and  $\text{Al}$  are completely separated. (See 1053.)
1069. MARCHAL and WIERNICH (*J. S. C. I.*, 1891, 1034).—To nearly neutral  $\text{H}_2\text{SO}_4$  solution, add  $\text{MnO}_2$  and boil;  $\text{Fe}$  is precipitated. Precipitate  $\text{Al}$  with  $\text{AmHO}$ , reduce  $\text{CrO}_3$ , and precipitate.
1070. MATIGNON (*J. C. S.*, l., 984).—In alkaline solutions  $\text{H}_2\text{O}_2$  immediately converts  $\text{Cr}_2\text{O}_3$  to  $\text{CrO}_3$ ; in acid solutions the easily decomposable per-chromic acid is formed.

## V. Detection of Chromium.

1071. STORER (*C. N.*, i., 253, etc.).— $\text{PbO}_2$  best reagent for effecting oxidation.  $\text{PbO}_2$ ,  $\text{MnO}_2$ , and  $\text{KMnO}_4$  form  $\text{CrO}_3$  in cold acid solutions;  $\text{PbO}_2$  (not  $\text{Pb}_3\text{O}_4$ ),  $\text{MnO}_2$ ,  $\text{KMnO}_4$ ,  $\text{Br}$ ,  $\text{I}$ ,  $\text{HgO}$ , and hypochlorite in alkaline solutions. Formation of perchromic acid with  $\text{H}_2\text{O}_2$  the most delicate reaction.
1072. NEVILLE (*C. N.*, xxxiv., 19).—Add ether and  $\text{H}_2\text{O}_2$  to  $\text{CrO}_3$  solution; a blue colour =  $\text{Cr}$ .  $\text{Ni}$ ,  $\text{Co}$ ,  $\text{Fe}$ ,  $\text{Mn}$ , and  $\text{Al}$  do not interfere; acetates do. The blue colour in ether is used as indicator (M'CULLOCH, *C. N.*, lv., 2) in estimating acidimetrically  $\text{K}_2\text{CrO}_4$  in the presence of  $\text{K}_2\text{Cr}_2\text{O}_7$ .

1073. REICHARDT (*J. S. C. I.*, 1901, 1241).—Perchromic acid test interfered with by V, Mo, and W.
1074. CAZENEUVE (*J. C. S.*, lxxviii., ii., 627).—Diphenylcarbazide in dilute HCl gives a violet colour with  $\text{CrO}_3$ . Detects one part per million.
1075. DONATH (*C. N.*, lix., 109).—Similar to 1039. Use KI and starch. Small quantities are estimated by precipitating with  $\text{Am}_2\text{S}$ .
1076. M'CAY (*C. N.*, lxxv., 221).—After fusing with  $\text{Na}_2\text{CO}_3 + \text{KNO}_3$  the yellow colour of the acidified extract looked for may have been destroyed by the nitrous acid present. (See 976.)
1077. TERRIEL (*C. N.*, xi., 136).—Precipitate the ferric solution with KHO, oxidize with permanganate, and add lead acetate and acetic acid to the filtrate. Traces of W, Mo, and Va in steel are similarly detected.
1078. WALDEN (*J. C. S.*, liv., 321).—Diphenylamine in concentrated  $\text{H}_2\text{SO}_4$  detects one part  $\text{K}_2\text{Cr}_2\text{O}_7$  in 700,000.

#### VI. Miscellaneous Notes.

1079. FRESSENIUS and HINTZ (*C. N.*, lxi., 65).—Scheme for very elaborate analysis of chrome-iron. The material is decomposed in a current of chlorine.
1080. CLARK (*J. S. C. I.*, 1895, 510).—Decompose ore with  $\text{KHSO}_4$  preparatory to estimation of  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Cr}_2\text{O}_3$ .
1081. MOISSAN (*C. N.*, lxx., 93).—Preparation, physical and chemical properties of metallic Cr.
1082. JANNASCH and VOGTHERR (*C. N.*, lxiv., 293).—Chromite decomposed with HCl in sealed tube.
1083. SCHNEIDER (*J. I. S. I.*, 1886, 399).—Fifty per cent FeCr would dissolve in HCl, if it were not for a protective coating of oily hydrocarbon.
1084. RIDEAL and ROSENBLUM (*C. N.*, lxxiii., 1).—Give prominence to  $\text{Na}_2\text{O}_2$  in a review of the means proposed for decomposing chromite, ferrochromium, etc. A bibliography of forty items.
1085. WARREN (*C. N.*, lxxv., 186).—Ferro-chromium is completely dissolved by hot concentrated  $\text{H}_2\text{SO}_4$  (see 1060). Borax in fusion mixtures contaminates the precipitates of the subsequent analysis.
1086. CARNOT and GOUTAL (*J. C. S.*, lxxii., ii., 555).—Chromium exists in steel as a Cr-Fe carbide.
1087. ZIEGLER (*J. S. C. I.*, 1893, 377).—Describes the following processes for steel:—Fusion of the dried residue; removal of the iron with cuprammonium chloride; fusion with  $\text{NaHSO}_4$ , or oxidation with  $\text{KMnO}_4$ ; and dissolving out other chlorides than Cr from the dried residue with alcohol.
1088. PROCTOR (*J. S. C. I.*, 1897, 413).—A review of the processes for estimating  $\text{CrO}_3$  and some mixtures of Cr salts.

1089. JERVIS (*C. N.*, lxxvii., 133).—Either acid or alkaline chromate solutions are reduced by filter paper. (See 992.)
1090. PARRY and MORGAN (*C. N.*, lxvii., 307).—There is no satisfactory process for estimating Cr in steel. Describes some processes the like of which are otherwise noticed.

## NICKEL.

The classification is :

- I. SEPARATION OF IRON.
  - a. By precipitating the iron—
    - (1) As Acetate ; (2) As Hydrate ; (3) Miscellaneous.
  - b. By precipitating the Nickel.
  - c. Electrolytic Separations.
- II. SEPARATION OF OTHER ELEMENTS.
- III. GRAVIMETRIC ESTIMATIONS.
  - a. As Oxide or Sulphide.
  - b. By Electro-deposition.
  - c. Miscellaneous.
- IV. VOLUMETRIC ESTIMATIONS.
  - a. With Potassium Cyanide.
  - b. Miscellaneous.
- V. DETECTION.
- VI. MISCELLANEOUS NOTES.

### I. Separation of Iron.

#### a. *By Precipitating the Fe:*

1. *By means of Acetates.*—The separation of nickel from iron by means of acetate requires greater manipulative precision than the like separation of any other element of the same group, and therefore a few references to papers which discuss the basis of acetate separations are included. (See also MANGANESE, p. 380.)

1091. MACKINTOSH (*C. N.*, lvi., 65).—Acetate separation needs to be repeated six times. Cobalt more difficult to separate than nickel. Precipitates Ni, Co, and Fe as sulphides, treats precipitate with HCl, and makes acetate separation of the soluble and insoluble portions.
1092. WESTERSON (*J. I. S. I.*, 1894, ii., 495).—Sample dissolved in  $H_2SO_4$ , oxidized, and Fe repeatedly precipitated. Mn interferes with electro-deposition of Ni.

1093. BREARLEY (*C. N.*, lxxiv., 16).—Precipitation from a solution containing 7 per cent. acetic acid. Ni titrated with KCN and AgI; copper separated as sub-sulphocyanide; SO<sub>2</sub> and KCNS do not interfere with titration of the Ni.
1094. DEBRAY (*C. N.*, xxi., 53).—Ferric acetate separates on boiling into acetic acid and colloidal oxide; the latter is insoluble in ammonium salts and acetic acid.
1095. BREARLEY (*C. N.*, lxxvi., 222, etc.).—Ease of separation of the following elements is in the order Mn, Zn, Co, Ni, Cu. Attempts to deduce reasons for this from the character of the salts separated. Separation of various elements without a second precipitation (*C. N.*, lxxvi., 49 and 222, Nickel; lxxvi., 165, Cobalt).
1096. GIBBS (*C. N.*, xi., 102).—Add enough acetate to convert all bases into neutral acetates to the cold solution.
1097. BREARLEY (*C. N.*, lxxix., 193).—It is best, according to both theory and practice, to add acetate to the boiling solution.

*a. 2. Precipitating Iron as Hydrate:*

1098. THOMAS (*C. N.*, xxxv., 187).—Repeated precipitation of the Fe with excess of ammonia.
1099. SLEEPER (*C. N.*, lxix., 15).—Decompose material with aqua regia, KBr and Br, or NaHSO<sub>4</sub>. Precipitate Ni and Fe with NaHO, dissolve in H<sub>2</sub>SO<sub>4</sub>, and *rapidly* add (NH<sub>4</sub>)HO to the *cold* solution. Detailed instructions for electro-deposition of the Ni.
1100. NEUMANN (*J. I. S. I.*, 1898, ii., 560).—The Fe is separated with (NH<sub>4</sub>)HO and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and the Ni electro-deposited from the filtrate.
1101. MOORE (*C. N.*, xlv., 76).—To faintly acid solution add (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and large excess oxalic acid; precipitate Fe with (NH<sub>4</sub>)HO.
1102. EMMENS (*J. I. S. I.*, 1893, i., 414).—Precipitated ferric hydrate boiled with dilute acid; only little Fe dissolves along with Ni; Ni and Co are electro-deposited. Applied to regulus, minerals, and alloys (*J. S. C. I.*, 1892, 1035).
1103. JUPTNER (*J. I. S. I.*, 1894, i., 616).—Precipitate with (NH<sub>4</sub>)HO in the presence of (NH<sub>4</sub>)Cl, and keep hot several hours. (Repeated precipitation is necessary, *J. I. S. I.*, 1894, ii., 495.) Ni and Co precipitated as sulphides, and Mn and Al separated.
1104. MOORE (*C. N.*, lxxv., 75).—The separation by NH<sub>4</sub>HO is worthless; by acetate needs four precipitations.
1105. IBBOTSON and BREARLEY (*C. N.*, lxxxix., 193).—Precipitated Fe<sub>2</sub>(HO)<sub>6</sub> adsorbs Ni from ammoniacal but not from acidified solutions, or from solutions of double nickel ammonium salts. Perfect separation on adding AmHO if only enough KCN to form Ni(CN)<sub>2</sub>. 2 KCN is present.
1106. ZIEGLER (*J. S. C. I.*, 1893, 377).—An acid solution of the metals is poured into an alkaline solution of ammonium borate. Ni, Co, and Cu are in solution; Fe, Al, and Mn are precipitated.

1107. BLOXAM (*C. N.*, lii, 109).—The precipitation of Fe with  $(\text{NH}_4)\text{HO}$  always carries down the Co in larger proportion than the Ni, so much so that Ni may in this way be roughly detected in the presence of cobalt.
1108. REINITZER (*C. N.*, xlviii, 114).—Solutions of  $\text{Cr}_2\text{O}_3$  when boiled with sodium acetate are not precipitated by alkalis, alkaline carbonates, phosphates, etc., and the same property is conferred on certain amounts of Fe or Al present therewith. RECOURA (*C. N.*, lxxviii, 46).—The presence of alkaline sulphites have a like effect.
- a. 3. Miscellaneous Processes.* (See also 307, 317, 319, 320, 321, 323.)
1109. MOORE (*C. N.*, liv., 300).—Add sodium phosphate, clear with acid, boil, and precipitate with acetate; precipitate Ni with KHO, and electro-deposit from sulphates. Shortcomings of Field's (320) Wöhler's (hydrate), and acetate processes enumerated.
1110. CHENEY and RICHARDS (*C. N.*, xxxvi., 161).—Acetate and hydrate inferior to Field's process. Precipitate with sodium phosphate from acetic solution; Ni electro-deposited; with more than 3 per cent. Ni, precipitation to be repeated.
1111. EASTWICK (*J. I. S. I.*, 1894, i., 615).—Depends on solubility of nickel sulphide and insolubility of iron sulphide in acid solution of  $(\text{NH}_4)_2\text{SO}_4$ . A little Fe goes with the nickel.
1112. GALBRAITH (*J. S. C. I.*, 1882, 345).—Precipitated with calcium sulphide; the Fe dissolved out with HCl; Ni weighed as sulphate.
1113. ROSENBLATT (*J. C. S.*, l., 492).—Ni and Co are separated from Fe, Cr, Al, Mn, and Zn by precipitating the latter elements with potassium thiocarbonate.
1114. ROTHE (*C. N.*, lxvi., 182).—Hydrochloric acid solutions of ferric salts are soluble in ether; similar solutions of NiO, MnO, FeO,  $\text{Cr}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$  are not; hence a means of separating them.
1115. SARGENT (*C. N.*, lxxxi., 209 and 240).—Estimation of Ni in steel based on 1114.
1116. SPELLER (*C. N.*, lxxxiii. 124).—Examination of some features of the Ether-HCl separation.
1117. PROCTOR-SMITH (*C. N.*, lxxxiii., 153).—Modified manipulation of the ether process for separating Ni from steel.
1118. NORRIS (*J. S. C. I.*, 1901, 551).—The ether separation is improved by the presence of Br and acetone.
1119. LANGMUIR (*J. S. C. I.*, 1900, 378).—Oxidize ore with  $\text{HNO}_3 + \text{Br}$ , separate Fe with AmHO, re-dissolve  $\text{Fe}_2(\text{HO})_6$  and separate remaining Ni with ether. Electro-deposit Ni from combined filtrates.
1120. BREARLEY (*C. N.*, lxxviii., 15).—Uses chromates instead of acetates. A large excess of the precipitant used in acetic solutions without any Ni being precipitated. Also separates Fe and Cu.



1121. NICOLARDOT (*C. N.*, lxxxiv. 256).—Fe is precipitated as basic sulphate free from Ni, Co, Mg, Zn, Cu, Mn, Cd, Cr, and Al. (See 307.)

*b. By Precipitating the Nickel:*

1122. THOMPSON (*C. N.*, vii., 185).—To acidulated sulphates of Ni, Co, Fe, Mn, Zn, and Cu add  $(\text{NH}_4)_2\text{SO}_4$ ; nearly all the Ni and Co separate as "alums" on standing.
1123. MOORE (*C. N.*, lvi., 3).—Add pyrophosphate until precipitate begins to re-dissolve; add excess KCN, boil, add KHO, and precipitate Ni with KHO and Br. Co remains with the iron; Ni estimated electrolytically. A modified process, leaving out pyrophosphate and embracing other separations (*C. N.*, lvii., 125).
1124. CAMPBELL and ANDREW (*J. I. S. I.*, 1895, ii., 598).—Add sodium pyrophosphate and carbonate; precipitate Ni with sodium xanthate; convert to sulphate and electro-deposit, or titrate with KCN and AgI. For preparation of xanthate see CAMPBELL (*J. C. S.*, lxxviii, ii., 577).
1125. PINERUA (*C. N.*, lxxv., 193).—Based on the insolubility of the chlorides of Ni and Al and the solubility of the chlorides of Co and Fe in etherized HCl are processes for the separation of Ni and Al from Fe and Co. (See 1114 and 1231.)
1126. PERILLON (*J. I. S. I.*, 1898, ii., 562).—Precipitate the dissolved sample with KHO, add oxalic acid, dry at  $80^\circ$ ; boil dried mass with dilute acetic acid and alcohol, and ignite the precipitated oxalate to NiO.
1127. CLASSEN (*C. N.*, xxxvi., 40).—In Wöhler's process for separating As and Ni (1152), if Fe is present the Co and Ni are completely precipitated on neutralizing, adding acetic acid, and potassium oxalate. (See 530.)
1128. MILLER and MATHEWS (*C. N.*, lxxxi., 282).—Iron is not precipitated as cobalti-cyanide in the presence of  $\text{Am}_2\text{SO}_4$ ; Ni, Co, Zn, and Mn are.

*c. Electrolytic Separations:*

1129. LE ROY (*C. N.* lxiii., 194) and HERRENSCHMIDT and CAPELLE (*C. N.*, lxix., 142).—Ni, Co, and Fe are deposited from a solution containing citric acid, ammonia, and ammonium sulphate; on reversing the current in an ammoniacal solution of  $(\text{NH}_4)_2\text{SO}_4$ , Fe is precipitated; Ni and Co are deposited together.
1130. DUCRU (*C. N.*, lxxvi., 279).—Electrolyze ammoniacal solution containing precipitated iron. A small amount of iron is deposited with the Ni. Mn, P, and large amounts of  $\text{Cr}_2\text{O}_3$  do not interfere.  $\text{CrO}_3$  prevents electro-deposition entirely.
1131. NEUMANN (*J. S. C. I.*, 1898, 1074).—On electrolyzing as above (1130) the deposited Fe varies with the amount in solution, time, strength of current, etc.
1132. ENGELS (*J. C. S.*, lxxiv., ii., 192).—The deposited Ni is free from iron if the latter has been oxidized with  $\text{H}_2\text{O}_2$ . (See also Foerster, *J. C. S.*, lxxiv., ii., 228.)

1133. VORTMANN (*J. C. S.*, lxvi., 34).—Zn, Co, and Fe are deposited free from Ni in an alkaline tartrate solution. Ni, Co, and Cu are estimated in presence of Fe, and after the manner of 1130.
1134. MARSHALL (*J. C. S.*, lxxviii., ii., 185).—A rise of potential may be taken as an indication that all the Ni has been deposited.

## II. Separating other Elements from Nickel.

*Cobalt.* (See 1206, etc.)

1135. *Zinc.* (See also 1113, 1181, 1182).—BRUNNER (*C. N.*, i., 95).—With  $H_2S$  from solution containing sodium acetate. Excess acetate and heat to be avoided. Ni and Co in solution.
1136. DOHLER (*J. C. S.*, lxxv., 811).—Precipitate Zn with  $H_2S$  in the presence of soda formate and formic acid.
1137. GIBBS (*C. N.*, xi., 149).—Add HCN gas and  $Na_2S$  to solution containing acetate, or precipitate hot solution with  $Na_2S$  and dissolve out Zn with HCl. The former process also separates Ur from Ni and Co.
1138. MOORE (*C. N.*, l., 151).—Precipitate with  $(NH_4)_2S$ , dissolve in KCN, and precipitate ZnS with soda acetate and acetic acid.
1139. TREADWELL (*J. C. S.*, lxxx., ii., 281).—Zn is precipitated with  $H_2S$  in the presence of  $AmCNS$ ,  $Am_2SO_4$ , or  $AmCl$ .
1140. VON BERG (*C. N.*, lv., 236).—Precipitated with  $H_2S$  from formic or monochloracetic solutions.
1141. HAMPE (*J. C. S.*, lii., 182).—As 1140. Monochloracetic acid the more efficient, especially with Co.
1142. BAUBIGNY (*C. N.*, lix., 88).—From acetic solutions with  $H_2S$  in the cold. Not available for cobalt (*J. C. S.*, lvi., 653).
1143. BEILSTEIN (*C. N.*, xxxix., 74).— $H_2S$  passed into cold ammoniacal solution made acid with citric; Zn precipitated. Electro-deposition of Ni made from solution of nitrates;  $(NH_4)Cl$  interferes.
1144. ALT and SCHULZE (*C. N.*, lxi., 124).—With  $H_2S$  from hot or cold solutions of succinic acid. Process for analyzing nickel-silver.
1145. *Zinc and Copper.*—CARNOT (*C. N.*, liii., 172 and 196).—Cu precipitated with hyposulphite. Zn from oxalic acid solutions with  $H_2S$ . Same process for cobalt.
1146. WÖHLER (*C. N.*, xxii., 84).—From acid solution of German silver precipitate Cu as  $CuCNS$ ; convert Ni and Zn to double cyanides; precipitate Zn with  $K_2S$  (not  $(NH_4)_2S$ ), and Ni from oxidized filtrate with KHO.
1147. MOORE (*C. N.*, lii., 20).—Analysis of German silver. Precipitate Cu from HCl solution with  $H_2S$ , add KCN to filtrate, and precipitate Zn with  $(NH_4)_2S$ . The Cu and Zn are electro-deposited.
1148. *Copper.*—DEWILDE (*C. N.*, vii., 49).— $H_2S$  always carries Ni down. Add cream of tartar, precipitate with KHO in alcohol, re-dissolve in

- excess, and precipitate Cu with glucose. The Ni, precipitated by KHO, after calcining and grinding, is easily washed free from potash salts.
1149. RICHE (*C. N.*, lxxvi., 241).—Ni-Cu alloys (coins) have the Cu deposited from acid solution of sulphates. Then Ni deposited from ammoniacal solution. Similar processes, ROBERTS (*J. C. S.*, l., 101) and LANGBEIN (*J. C. S.*, l., 1077).
1150. CLASSEN (*J. C. S.*, xlvi., 191).—Cu electro-deposited from ammonio-oxalates.
1151. KAIKOW (*J. C. S.*, lxviii., ii., 246).—Cu precipitated with hydrazine hydrochloride and KI. Ni, Cd, and Zn are in solution.
1152. *Arsenic*.—WÖHLER (*C. N.*, xxxv., 141).—Both metals precipitated with  $\text{Na}_2\text{CO}_3$ , digested with oxalic acid, and Ni or Co oxalates filtered off.
1153. JANNASCH and LEHNERT (*J. C. S.*, lxx., ii., 547).—Co and Ni are precipitated from alkaline solution with  $\text{H}_2\text{O}_2$ .
1154. *Cadmium*.—SMITH and WALLACE (*J. C. S.*, lxii., 920).—Cd electro-deposited after adding KHO. Also RUDORFF (*J. C. S.*, lxiv., ii., 305) and SMITH and MOYER (*J. C. S.*, lxiv., ii., 496). Ni is precipitated in acid solution if a strong current is employed.
1155. *Bismuth*.—SMITH and MOYER (*J. C. S.*, lxiv., ii., 497).—Electrolytic.  $\text{H}_2\text{SO}_4$  preferable to  $\text{HNO}_3$  solutions.
1156. JANNASCH and ROSE (*J. C. S.*, lxvi., ii., 482).—Separation in ammoniacal solution with  $\text{H}_2\text{O}_2$ .
1157. *Mercury*.—SMITH and FRANKEL (*J. C. S.*, lviii., 664).—Electro-separation of Hg and Ag from Ni and Co. Also HEIDENREICH (*J. S. C. I.*, 1896, 774) and RUDORFF (*J. C. S.*, lxvi., ii., 399).
1158. *Gold*.—SMITH and MUHR (*J. C. S.*, lx., 1398).—Electro-separation from cyanide solutions.
1159. *Aluminium*.—GONTIERE (*J. S. C. I.*, 1896, 830).—The metallic Al is dissolved in NaHO. The Ni is separated from the residual metals (Cu, Pb, Fe) by electrolysis and precipitation with ammonia.
1160. LEFFLER (*C. N.*, lxxvii., 265).—Al precipitated with sodium phosphate in acetic acid solutions.
1161. *Lead*.—JANNASCH and LESINSKY (*J. C. S.*, lxvi., ii., 33).—Precipitated from ammoniacal solution with  $\text{H}_2\text{O}_2$ .

### III. Gravimetric Estimation of Nickel.

#### a. As Oxide or Sulphide :

1162. HADOW (*C. N.*, ii., 85).—Ni separated from solution of the ore with  $\text{CaCO}_3$  and acetate ; Ni and Co precipitated with  $\text{H}_2\text{S}$  and converted into sulphates, or precipitated with KHO or binoxalate and weighed as oxides. Filter-paper absorbs Ni and Co from strong solutions of the acetates.

1163. GIBBS (*C. N.*, xvii., 172).—Ni is completely precipitated by a small excess of  $\text{Na}_2\text{CO}_3$  and boiling. Ignited to oxide.
1164. SCHMIDT (*C. N.*, lxx., 248).—Precipitated by  $\text{H}_2\text{S}$  from an  $(\text{NH}_4)\text{NO}_3$  solution. The sulphide converted to oxide by ignition with ammoniacal mercuric cyanide.
1165. ROSE (*C. N.*, ii., 302).—Neither Ni nor Co can be estimated as sulphide by heating with S in H, as iron, Mn, Zn, and Cu may.
1166. FRESSENIUS (*C. N.*, iv., 150).— $(\text{NH}_4)_2\text{S}$  precipitates Ni slowly and not completely;  $(\text{NH}_4)\text{Cl}$  assists,  $(\text{NH}_4)\text{HO}$  retards, the precipitation.
1167. LECREUIER (*J. C. S.*, lviii., 297).—The retention of nickel sulphide in solution is due to the formation of a thionickelate.
1168. TERREIL (*J. C. S.*, lxii., 1132).— $\text{H}_2\text{S}$  precipitates Ni and Co in the presence of many organic salts and sulphur and phosphorous acids.
1169. BAUBIGNY (*C. N.*, xlv., 174 and 229).—Precipitation of NiO salts with  $\text{H}_2\text{S}$  depends on the ratio weight of acid to weight of metal, and not weight of acid to weight of water. This distinction serves to separate other metals (*e.g.* Zn). (See also *C. N.*, xlv., 257.) For action of  $\text{H}_2\text{S}$  on  $\text{NiSO}_4$  in acetic solutions see *C. N.*, xlvi., 17; for action on  $\text{NiCl}_2$ , see *C. N.*, xlvi., 40; action on Co salts, *J. C. S.*, liv., 113.

*b. By Electro-deposition.* (See also 1099, 1100, 1102, 1109, 1110, 1123.)

1170. MERRICK (*C. N.*, xxiv., 100, 172).—Cu and Ni may be successively deposited from the same solution. Only a limited number of salts are suitable for electro-deposition (*C. N.*, xxvi., 209).
1171. FRESSENIUS and BERGMANN (*C. N.*, xlii., 75).—Co and Ni not deposited if solution contains free mineral acids. Solutions of  $(\text{NH}_4)_2\text{SO}_4$  (no  $\text{NH}_4\text{Cl}$ ) are best. Sulphocarbonate used to indicate when precipitation is complete.
1172. RUDORFF (*J. C. S.*, lxiv., ii., 94).—From sulphate or pyrophosphate solutions.
1173. CLASSEN (*J. C. S.*, xlviii., 191).—Ni, Co, and Fe deposited from double oxalates. Fe estimated volumetrically, Ni by difference; Co separated with nitrite.
1174. BRAND (*J. C. S.*, lviii., 294).—From ammoniacal solution of the pyrophosphates.
1175. KOHN and WOODGATE (*J. S. C. I.*, 1889, 256).—From various solutions. Table of metals which can be determined quantitatively, and references.
1176. CLASSEN (*J. C. S.*, lxvi., ii., 481).—Particulars of current density, potential, etc., for deposition of Ni and other elements.
1177. WOLMAN (*J. C. S.*, lxxiv., ii., 50).—Oxalate (1173) and pyrophosphate (1172) solutions lead to high results.
1178. LANGBEIN (*C. N.*, lvii., 251).—The deposit from solutions containing Mn are contaminated thereby. (See also 1092.)
1179. RICHE (*C. N.*, xxxvi., 96).—Deposition from ammoniacal solution carries down Mg. Purified by re-deposition.
1180. CETTEL (*J. S. C. I.*, 1895, 69).—From ammoniacal solution of chlorides.

*c. Miscellaneous Processes:* (See also 1112, 1162.)

1181. FRESSENIUS (*C. N.*, xxix., 193).—Ore, etc., decomposed by acid or bisulphate, Schwarzenberg (311) separation of Fe. Ni and Co precipitated with  $H_2S$ , with  $KHO$ , and finally reduced to metal in hydrogen. (See also *C. N.*, xxx., 16.) Zn separated by volatilizing with  $(NH_4)Cl$ , and Co as nitrate.
1182. BAYLEY (*J. S. C. I.*, 1887, 449).—Add  $(NH_4)_2S$  to alkalinity, ammonium benzoate, and  $HCl$ ; the precipitated sulphide weighed as sulphate; Zn separated in a solution containing phosphoric acid.
1183. CLARKE (*J. S. C. I.*, 1896, 866).—To solution containing ammonium phosphate add  $HCl$  to neutrality, then 20 per cent. alcohol. Precipitate ignited to pyrophosphate. Zn is estimated similarly. (See also 1225.)

#### IV. Volumetric Estimation of Nickel.

*a. Titration with Potassium Cyanide.* (See also 1093, 1124.)

1184. LECŒUVRE (*C. N.*, lxxi., 188).—Feebly alkaline solution titrated with  $KCN$  until the precipitate first formed just re-dissolves;  $NH_3$  salts or small amounts of  $(NH_4)HO$  do not interfere.
1185. MOORE (*C. N.*, lix., 160).—Titrate in ammoniacal solution, using cupric ferro-cyanide indicator. Sulphates, nitrates, chlorides, and acetates do not interfere.
1186. CAMPBELL (*C. N.*, lxix., 139).—Fe separated as phosphate in acetic solution. Separate Cu with Pb, and then Pb and Mn as phosphate. Deposit Ni electrolytically or titrate with  $KCN$ , as in 1185. How to prepare the indicator.
1187. MOORE (*C. N.*, lix., 292).—Mn and large amounts of ammonium salts interfere with (1185). By adding pyrophosphate to acid solution until precipitate re-dissolves and titrating ammoniacal solution, neither Fe, Al, Zn, nor Mn interfere.
1188. DENIGES (*C. N.*, lxix., 42).—General method for estimation of Ag, in which  $KI$  is added to form indicator in ammoniacal solution. (This very suggestive paper should be read along with the processes for estimating Ni based on the same principle).
1189. MOORE (*C. N.*, lxxii., 92).— $KCN$  added until clearing of the suspended  $AgI$  indicates the formation of  $Ni(CN)_2 \cdot 2KCN$ . The  $KCN$  may be standardized with Ni or Ag; Co is estimated with the Ni; Mn, Cu, and Zn interfere; Zn, Al, Fe, or Mg kept in solution with pyrophosphate or an organic acid.
1190. BREARLEY and JERVIS (*C. N.*, lxxviii., 77, etc.).—Some points in the cyanometric estimation. Interferences exerted by a score elements, and means of avoiding them. Estimation in presence of elements giving precipitates in alkaline solutions.

*b. Miscellaneous Volumetric Processes :*

1191. KUNZELL (*C. N.*, viii., 38).—Hot ammoniacal solution titrated with sodium sulphide, using silver or nitro-prusside as indicator. Titration may be made in presence of Cu.
1192. SYSSOYEFF (*J. I. S. I.*, 1893, i., 414).—Precipitate  $\text{Ni}_2\text{O}_3$  with Cl from a KCN solution ; the Ni is calculated from the reaction—  

$$\text{Ni}_2\text{O}_3 + \text{H}_2\text{O}_2 = 2 \text{NiO} + \text{H}_2\text{O} + \text{O}_2$$
after measuring the oxygen. Iron kept in solution as ferrocyanide.
1193. GIORGIS (*J. C. S.*, lxxv., 452).—Gibb's process, precipitating with alcoholic oxalic solution, is inaccurate. Precipitate with oxalic solution of Sr or Ba oxalate, and titrate either the dissolved precipitate or the excess of precipitant with permanganate.
1194. LUCAS (*C. N.*, lxxx., 38).—Separate Fe with ammonia and  $(\text{NH}_4)\text{Cl}$ , add K sulphocarbonate, and compare red colour formed with standards ; Co can be detected by using ammonium sulphocarbonate at the same time.
1195. SPULLER (*J. I. S. I.*, 1897, ii., 507).—Fe precipitated with ZnO ; the filtrate colorimetrically compared with standards. FIEBER (*J. S. C. I.* 1900, 563), similarly, but precipitates with AmHO.

**V. Detection of Nickel.**

1196. ALLEN (*C. N.*, xxiii., 290).—Add  $(\text{NH}_4)\text{Cl}$ ,  $(\text{NH}_4)\text{HO}$ , and ferricyanide ; a red colour = Co ; no change but a red precipitate on boiling = Ni. (See also CARTER, *C. N.*, xlvii., 273.)
1197. DAVIES (*C. N.*, xxxii., 44).—After detecting Co with ferricyanide, add ferrocyanide and HCl ; a precipitate = Ni ; detects 0.01 per cent. ; ferrocyanide may be used to detect Co also.
1198. DONATH and MAYRHOFER (*C. N.*, xlv., 46).—Precipitate with NaHO and I, dissolve out Ni with ammoniacal  $(\text{NH}_4)\text{Cl}$ , and detect with  $(\text{NH}_4)_2\text{S}$ . Boil HCl solution of the residue with KHO ; blue liquid = Co.
1199. VILLIERS (*C. N.*, lxxi., 45 and 49).—Tartaric acid, NaHO, and  $\text{H}_2\text{S}$  added successively. The colour of the filtrate indicates traces of Ni.
1200. CAVALLI (*J. C. S.*, lxxii., 603).—Precipitate with nitroprusside and treat with  $(\text{NH}_4)\text{HO}$  ; only the Ni compound dissolves.

**VI. Miscellaneous Notes.**

1201. PATTINSON (*C. N.*, viii., 136).—Ni and Co exist in small amounts in Cleveland ironstone.
1202. WARREN (*C. N.*, lv., 37).—Certain metallic adulterations of cube Ni render the metal non-magnetic, and may thus be detected.
1203. FLEITMANN (*C. N.*, lxx., 280).—Commercially pure nickel contains more or less Fe, Cu, Co, Zn, and Mn. Instructions for quantitative estimation of these.

1204. CETTEL (*C. N.*, lviii., 48).—Analysis of nickel-silver and separation of Sn, Pb, Cu, Zn, Fe, and Mn. Ni electro-deposited.
1205. CARNOT and GOUTAL (*J. C. S.*, lxxii., ii., 555).—Nickel is probably simply mixed with, or dissolved in, the iron.

## COBALT.

The arrangement is :

### I. SEPARATION OF NICKEL.

- a. Depending on behaviour with KCN.
- b. " " " oxidizing reagents.
- c. As Phosphate.
- d. Miscellaneous.

### II. SEPARATION OF OTHER ELEMENTS.

### III. GRAVIMETIC ESTIMATIONS.

### IV. VOLUMETRIC ESTIMATIONS.

- a. Oxidimetric.
- b. Miscellaneous.

### V. DETECTION OF COBALT.

#### I. Separating from Nickel.

##### a. Depending on Behaviour with KCN:

1206. GIBBS (*C. N.*, xi., 125).—By using a solution of HgO in KCN to precipitate Ni from the double cyanide of Ni and Co, the separation is immediate and complete ; the precipitates may be ignited and weighed at once ; Co determined by difference. Separation with KNO<sub>2</sub> lengthy and difficult.
1207. HADOW (*C. N.*, ii., 86).—In Liebig's process KCN should be added *before* the KHO ; SiO<sub>2</sub> should be absent. Precipitation of the Ni by Cl or a salt of Hg preferable to HgO. If cobalt is finally precipitated with HgNO<sub>3</sub> (Wöhler's process), chlorides and sulphates should be absent.
1208. FLECK (*C. N.*, xiii., 299).—NH<sub>3</sub> solution exposed to air (NH<sub>4</sub>)<sub>2</sub>S added, NH<sub>3</sub> evaporated, and KCN added ; the nickel sulphide dissolves.
1209. GUYARD (*C. N.*, xxxiv., 255).—Precipitate as sulphides, dissolve out Ni with KCN, acidulate filtrate, and ignite precipitated nickel cyanide to oxide.
1210. JORISSEN (*C. N.*, xlv., 240).—Precipitate with NaHO and Br, and dissolve out Ni with KCN ; not good for much Ni and little Co.

*b. Depending on Behaviour of Oxidized Compounds:*

1211. FLEISCHER (*C. N.*, xxii., 96).—Add hypochlorite and KHO, boil until precipitate is black, then dissolve out  $\text{Ni}_2\text{O}_3$  with  $(\text{NH}_4)\text{HO}$ .
1212. DONATH (*C. N.*, xlvii., 248).—Halve the solution; precipitate both metals as sesquioxides in one, and Co alone with KHO and I in the other; distil each precipitate with HCl and estimate the Cl with KI and hyposulphite.
1213. DELVAUX (*C. N.*, xliii., 196).—Dissolve oxides or sulphides in aqua regia, add  $(\text{NH}_4)\text{HO}$  and permanganate, then KHO to precipitate the Ni. The precipitate must be separated from Mn.
1214. VORTMANN (*C. N.*, xlix., 150).—Uses hypochlorite instead of permanganate (1213); detects traces of either metal in the other. (See also 1123.)
1215. M'CULLOCH (*C. N.*, lvi., 27).—Examination of Fleischer (1211) and Donath (1212) processes. The Co is not oxidized to  $\text{Co}_2\text{O}_3$ . Nickel salts precipitated with NaHO and an oxidizing reagent varied from  $\text{Ni}_6\text{O}_7$  to  $\text{Ni}_3\text{O}_4$ .
1216. BAYLEY (*C. N.*, xxxix., 81, and lxxxii., 179).—Ni and Co are not oxidized by hypochlorite to  $\text{Ni}_2\text{O}_3$ , but to  $\text{Ni}_3\text{O}_5$  and  $\text{Co}_3\text{O}_5$ , which are further decomposed on boiling.
1217. ARNOLD (*Steel Works Analysis*, p. 166).—By precipitating with Br and NaHO, the compound formed contained only about 15 per cent.  $\text{Ni}_2\text{O}_3$ .
1218. CARNOT (*C. N.*, lix., 183).—Co precipitated by  $\text{H}_2\text{O}_2$  and KHO is exactly  $\text{Co}_2\text{O}_3$ ; precipitated by hypochlorite, Br, or I, the proportion of O is greater; under the latter conditions, the Ni is exactly  $\text{Ni}_2\text{O}_3$ . Estimation and separation of the metals based on these facts. M'CULLOCH (*C. N.*, lix., 205) disputes the fundamental facts, and (*C. N.*, lix., 208) makes unsuccessful attempts to separate the metals after oxidation in ammoniacal solution.
1219. FISCHER (*J. C. S.*, lvi., 653).—Alkaline solution boiled with  $\text{H}_2\text{O}_2$ , and the oxygen in the  $\text{Co}_2\text{O}_3$  estimated with KI and  $\text{Na}_2\text{S}_2\text{O}_3$ .
1220. CARNOT (*C. N.*, lx., 54).—To acid solution add  $(\text{NH}_4)\text{HO}$  and  $\text{H}_2\text{O}_2$ ; or precipitate ammonio-cobalt molybdate from acetic solution with  $(\text{NH}_4)_2\text{MoO}_4$ ; Ni in solution; Zn and Cu do not interfere. A good way of detecting cobalt.
1221. TERREIL (*C. N.*, xiii., 133).— $\text{KMnO}_4$  added to hot ammoniacal solution, and then a faint excess of HCl; after a time, roseo-cobaltic hydrochlorate is precipitated. Detects 0.01 per cent. Co in Ni.

*c. Separation as Phosphate:*

1222. DIRVELL (*C. N.*, xl., 268).—Co precipitated by microcosmic salt and ammonium acetate as  $\text{NH}_4\text{O} \cdot 2\text{CoO} \cdot \text{PO}_5 + 2\text{H}_2\text{O}$  and ignited to pyrophosphate. The method is rapid.
1223. HOPE (*J. S. C. I.*, 1890, 375).—Uses process 1222 with electro-estimation for analysis of ores, mattes, etc.



1224. CLARKE (*C. N.*, xlviii., 262).—A careful examination of Dirvell's process. Accurate results with any proportion of Co and Ni. Process considerably modified.
1225. CLARKE (*J. S. C. I.*, 1896, 867).—Dirvell's process does not precipitate Co if present as cobaltic salt, and therefore by means of Br and  $\text{H}_2\text{O}_2$ , and the process (1183) Ni is precipitated in the presence of Co.

*d. Miscellaneous Processes for Separating Ni and Co :*

1226. FLEITMANN (*C. N.*, xxxii., 260).— $\text{KNO}_2$  fails to separate 1 per cent. Co from Ni. The Co is precipitated along with a little Ni by means of hypochlorite, and then the nitrite separation of the Co made.
1227. BAUBIGNY (*C. N.*, lxiv., 224).—Ba, Ca, Sr, and Pb interfere with the nitrite separation.  $\text{KNO}_2$  should always be tested for Pb.
1228. ILINSKI and KNORRE (*C. N.*, li., 170).—Precipitate cobalt with nitroso- $\beta$ -naphthol, ignite with oxalic acid, and reduce to metal; Fe and Cr must be absent (see 323 and 324). Also JANDA (*J. I. S. I.*, 1900, ii., 581).
- C. N.*, lii., 301.—Cobalti-nitroso- $\beta$ -naphthol is permanent in the presence of acids, alkalis, and oxidizing and reducing agents; stability with various reagents, and means of preparing the nitroso- $\beta$ -naphthol given.
1229. KNORRE (*J. C. S.*, xlviii., 840; and lxiv., ii., 500).—Scheme for analysis of commercial Ni: separation as above; cobalt ignited to  $\text{Co}_3\text{O}_4$ .
1230. PHIPSON (*C. N.*, xxxvi., 150).—Co and Ni are precipitated together by potassium xanthate; on making slightly ammoniacal, the Ni passes into solution.
1231. HAVENS (*C. N.*, lxxviii., 323).—Pinerua's process (1125) does not effect a complete separation. Part of the cobalt, if present in considerable amount, goes down with the Ni.
1232. ROSENHEIM and HULDSCHINSKY (*J. S. C. I.*, 1901, 840).—To concentrated solution add AmCNS and extract with ether-amyl-alcoholic mixture until  $\text{Co}(\text{SCN})_4$  is removed.
1233. GUCCI (*J. C. S.*, l., 1077).—Mixed sulphides are fused with  $\text{KNO}_3$ ; from the oxides, undissolved by water leaching, Ni is completely dissolved by 1.20  $\text{HNO}_3$ .
1234. BAUBIGNY (*C. N.*, lvii., 55).— $\text{H}_2\text{S}$  does not precipitate all the Co before acting on the Ni, in an acetic solution, as has been stated, and therefore no process on these lines is quantitatively available. (See 1169.)
1235. CLARKE (*C. N.*, xx., 154); and BROWNING and HARTWELL (*C. N.*, lxxxii., 203).—Metals precipitated with ferri-cyanide from  $(\text{NH}_4)\text{Cl}$  solution; nickel dissolved from precipitate with  $(\text{NH}_4)\text{HO}$ ; cobalt absolutely insoluble; process given as qualitative.
1236. HERRENSCHMIDT (*C. N.*, lxix., 112, etc.).—Cyanide superior to nitrite method of separation. Traces of Ni can be microscopically detected in cobalt hydroxide; weigh Ni and Co together as sulphates; determine Ni separately as sulphate after separating with KCN, Br, and

Cl; Co by difference. Discusses (p. 128) Baubigny's separation of Zn (1142); reviews experiments on the state of oxidation when Ni and Co are treated with oxidants in alkaline solution. Carbon monoxide (Mond's process) is recommended for the absolute separation of Ni and Co.

1237. KRAUSS (*C. N.*, lxiii., 254, etc.).—An examination of fourteen methods founded on the different behaviour of the higher oxides of the metals; two depending on the behaviour of the sulphides, Dirvell's process (1222) and Clarke's modification of it (1224); and six methods based on various principles. This memoir practically covers the whole ground up to 1891.
1238. BALACHOWSKY (*C. N.*, lxxxiv., 24).—Electro-separation.

## II. Separation of Cobalt from other Elements.

1239. Zinc.—VORTMANN (*J. C. S.*, lxviii., ii., 89).—Electro-deposition of Co from alkaline tartrate solution.
1240. WALLER (*J. S. C. I.*, 1897, 1043).—A summary of proposed means of making the electro-separation. (See also 1113, 1135, etc.)
1241. Bismuth.—JANNASCH and KAMMERER (*C. N.*, lxxii., 91).—On pouring a nitric acid solution of the metals into ammoniacal  $H_2O_2$ , Bi is precipitated.

## III. Gravimetric Estimation of Cobalt.

1242. GIBBS (*C. N.*, xvii., 172).—Neutral solution boiled with sodium acetate and hypochlorite. The  $Co_2O_3$ , reduced to Co in H, is free from alkali; Ni may be similarly estimated; this is Popp's process.
1243. GIBBS (*C. N.*, xxviii., 51).—Co converted to cobalti-cyanide, precipitated with  $HgNO_3$ , and  $HgO$ , ignited in air, and then reduced to metal in H.
1244. RUSSELL (*C. N.*, vii., 43).—Ignition in a powerful blast blowpipe and cooling in a current of  $CO_2$  forms true protoxide of cobalt.
1245. SALVETAT (*C. N.*, x., 91).—Oxide is calcined with a salt of Al, leaving a known residue. The increase in weight represents protoxide of cobalt.
1246. FRESENIUS (*C. N.*, iv., 150).— $(NH_4)_2S$  does not precipitate dilute Co solutions;  $NH_4Cl$  assists,  $(NH_4)HO$  slightly retards, precipitation.
1247. MOORE (*C. N.*, lxxv., 75).—Decompose Mn ores by fusion; precipitate Ni and Co as sulphides, convert to sulphates, and electro-deposit; separate Co by precipitation as ammonic phosphate. A rapid process is based on the absorption of oxygen by ammoniacal solutions of cobalt according to the equation  $2CoO + O = Co_2O_3$ .
1248. DAKIN (*C. N.*, lxxxiii., 37).—Critical examination of phosphate process. Precipitate may be weighed either as the ammonium phosphate or pyrophosphate. (See 1222, etc.)

## IV. Volumetric Estimation of Cobalt.

*a. Oxidimetric Processes :*

1249. WINKLER (*C. N.*, x., 215).—Co may be estimated in presence of Ni by precipitating with HgO and a standard solution of  $\text{KMnO}_4$ ; recognizes 0.1 per cent Co in Ni; oxygen compounds of Cl, S, As, and P interfere; As and P eliminated by adding  $\text{Fe}_2\text{Cl}_6$  and precipitating with HgO.
1250. DONATH (*C. N.*, xli., 15).—Modified Fleischer's process (1211). In one portion converts to  $\text{Co}_2\text{O}_3$  and  $\text{Ni}_2\text{O}_3$  with bromine, and in another to  $\text{Co}_2\text{O}_3$  and NiO with KHO and boiling. Each precipitate is distilled with HCl.
1251. M'CULLOCH (*C. N.*, lix., 51).—Measures the oxygen necessary to convert cobalto- to cobalti-cyanide; the operation is performed in absence of air and at barometric pressure. Ni, Mn, Pb, P, As, Al, Zn, Sb, Mo, and Ur do not interfere; Cu and Fe do.
1252. MOORE (*C. N.*, lxviii., 295).—The change from cobalto- to cobalti-cyanide either in alkaline or acid solutions is accompanied by greater absorption of O than is expressed by the usual equation,  $2\text{K}_4\text{CoCy}_6 + \text{H}_2\text{O} + \text{O} = \text{K}_6\text{Co}_2\text{Cy}_{12} + 2\text{KHO} + \text{H}_2\text{O}$ .
1253. JOB (*C. N.*, lxxviii., 254).—Alkaline cobalt solutions peroxidized with  $\text{H}_2\text{O}_2$ , and the  $\text{Co}_2\text{O}_3$  formed titrated with a ferrous solution.
1254. MOORE (*C. N.*, lxxxii., 66).—Dissolve ore in HCl, precipitate Fe with  $\text{AmCl} + \text{AmHO} + \text{Na}_2\text{CO}_3$  without making the solution alkaline (see 1105). Precipitate Co finally with  $\text{H}_2\text{O}_2$  and KHO, digest with KI, and titrate with hypo. (See 1216.)  
*C. N.*, lxxxii., 73).—Small amounts of Co are separated from Ni with Br and ZnO, the precipitate re-dissolved, and Co estimated as above.
1255. KARSLAKE (*J. C. S.*, lxiv., ii., 194).—Precipitate as cobalti-nitrite, boil with KHO, and titrate with permanganate; the oxidation is from the nitrous acid of the  $\text{K}_3\text{Co}(\text{NO}_2)_6$  to nitric acid.
1256. JOLLES (*J. C. S.*, lvi., 798).—The cobaltous solution is run into a measured volume of manganate until the latter is decolourized;  $\text{CoMnO}_3$  is precipitated.
1257. REIS and WIGGERT (*J. C. S.*, lx., 620).—Oxidation to cobaltic oxide with permanganate in presence of ZnO; excess of  $\text{KMnO}_4$  titrated with arsenious acid.
1258. PURGOTTI (*J. C. S.*, lxxii., ii., 77).—After converting to the sesquioxides, either Ni or Co may be estimated by titrating with a solution of the blue oxide of molybdenum ( $\text{Mo}_3\text{O}_8$ ). (See also *C. N.*, xxxviii., 22.)
1259. ROSSLER (*C. N.*, xli., 184).—Cobaltous solution mixed with standard silver and KHO solution;  $\text{Ag}_4\text{OCo}_2\text{O}_3$  is precipitated. Proceed thence as for Mn (532). Ni causes low results.

*b. Miscellaneous Processes :*

1260. NEUMANN (*J. C. S.*, lxviii., ii., 64).—Either Ni or Co estimated by titration with sodium sulphide.

1261. KRIEDER (*J. C. S.*, lxxviii., ii., 534).—The HCl solution of the ore precipitated with chalk, and a fraction of the filtrate colorimetrically compared with standard cobaltous chloride solution.
1262. BREARLEY (*C. N.*, lxxvi., 165).—Cyanometric estimation, using the AgI indicator as for Ni (1189).
1263. HARRIS (*J. C. S.*, lxxiv., ii., 487).—A criticism of Winkler's (1249), M'Culloch's (1251), Fleischer's (1211), Donath's (1250), and von Reis's methods. None of them quite satisfactory.

### V. Detection of Cobalt.

1264. BRAUN (*C. N.*, xii., 58).—KNO<sub>2</sub> and acetic acid added to a solution of Co in KCN gives a deep red solution.
1265. SKEY (*C. N.*, xv., 111).—In an ammoniacal solution in tartaric or citric acid ferri-cyanide produces a dark red colour. Can detect one part in 400,000. *C. N.*, xv., 328.—Any other acid may be substituted for tartaric. (See 1196.)
1266. REICHEL (*C. N.*, xliii., 7).—The KHO precipitate of the Ni and Co is heated with KHO (solid) and a little H<sub>2</sub>O. The Co dissolves with a blue colour, and may be precipitated from the filtrate with ether.
1267. TATTERSALL (*C. N.*, xxxix., 66).—Add KCN and yellow (NH<sub>4</sub>)<sub>2</sub>S; blood red=Co; only Cu interferes. PAPASOGLI (*C. N.*, xxxix., 149) says this test is most sensitive when the (NH<sub>4</sub>)<sub>2</sub>S is superstratified.
1268. PAPASOGLI (*C. N.*, xli., 74).—The previous reaction and a red colour formed when Zn is added to the double Ni and K cyanide are used to detect the one metal in the presence of the other.
1269. PAPASOGLI (*J. S. C. I.*, 1899, 74).—Saccharose and soda give a violet colour with one part Co in 50,000; further tests with amylsulpho-carbonate, etc., are applied when Ni is also present.
1270. MOORE (*C. N.*, lxxviii., 295; and lxxi., 81).—Investigates the cause of the red colour used by Papasogli (1268) as a test for Ni.
1271. BALL (*C. N.*, lxx., 36).—Pour a little of the solution on to anhydrous thiosulphate and heat; green colour=Co. Ni, Fe, Mn, etc., do not interfere.
1272. DURRANT (*C. N.*, lxxiii., 228).—Na<sub>2</sub>CO<sub>3</sub> + H<sub>2</sub>O<sub>2</sub> give a green liquid with Co in presence of much Ni.
1273. COEHN (*J. S. C. I.*, 1898, 605).—Co is detected in presence of Ni by its deposition in the fine cracks of a glass tube (stenolysis).
1274. VON ILINSKI (*J. C. S.*, lxx., ii., 451).—Add fresh nitroso-β-naphthol to HCl solution; dark red precipitate=Co. Works well in the presence of Ni.
1275. WOLFF (*C. N.*, xlvii., 94).—Fe precipitated from solution of the sulpho-cyanides with Na<sub>2</sub>CO<sub>3</sub>. Shake the filtrate with amyl alcohol and ether; cobalt is distinguished with the spectroscope by the absorption band between C and D.

1276. BETTINK (*J. S. C. I.*, 1899, 519).—To detect Co in Fe treat the solution with KCNS and  $\text{Na}_2\text{S}_2\text{O}_3$  until the red colour disappears, filter, and add alcohol-ether; a blue colour indicates Co. See also DITZ (*J. S. C. I.*, 1901, 389); and TREADWELL (*Ibid.* 390).
1277. JAWOROWSKI (*J. C. S.*, lxxv., 61).—Add sodium pyrophosphate to neutral solution, dilute till solution is colourless, add  $\text{Na}_2\text{CO}_3$  and Br; a reflected green colour indicates cobalt.

## TUNGSTEN.

The arrangement is :

- I. SEPARATION FROM OTHER ELEMENTS.
- II. GRAVIMETRIC ESTIMATIONS.
- III. VOLUMETRIC ESTIMATIONS.
- IV. DETECTION AND MISCELLANEOUS NOTES.

### I. Separation from Other Elements.

1278. *Iron*.—BENNEVILLE (*J. I. S. I.*, 1895, i., 205).—Fuse with  $\text{Na}_2\text{CO}_3$ ,  $\text{KNO}_3$ , and  $\text{NaHO}$ ; extract with water, and evaporate with  $\text{HCl}$ . Fe and Mo are also separated by fusion. (See 1331 and 1332.)
1279. *Silicon*.—SKEY (*C. N.*, xvii., 165).—Hydrous  $\text{SiO}_2$  is sensibly dissolved in ammonia, and is partly soluble even after strong ignition. PIBRAM (*C. N.*, xvii., 227) determines the solubility of variously treated silica in ammonia.
1280. VIGOUROUX (*C. N.*, lxxviii., 291).—Silicide of tungsten is analyzed by heating with chlorine. The silicon chloride is volatilized and finally weighed as  $\text{SiO}_2$ .
1281. WADDELL (*C. N.*, l., 113).—By fusion with  $\text{KHSO}_4$ , etc.; also with ammonia.
1282. BENNEVILLE (*J. S. C. I.*, 1897, 636).—Several evaporations with HF are sometimes necessary to remove all the  $\text{SiO}_2$  from  $\text{WO}_3$ . Accurate separation with ammonia not possible.
1283. HERTING (*C. N.*, lxxxiv., 75).— $\text{WO}_3$  goes off on treating  $\text{WO}_3 + \text{SiO}_2$  with HF. Fuse with  $\text{KHSO}_4$ , and digest with  $\text{Am}_2\text{CO}_3$ .
1284. M'KENNA (*Ibid.*) denies volatility of  $\text{WO}_3$ , and so do WELLS and METZGER (*C. N.*, lxxxiv., 3), whether  $\text{H}_2\text{SO}_4$  is present or not; but  $\text{WO}_3$  is volatilized if heated alone over a blast lamp.
1285. *Tin*.—RAMMELSBERG (*C. N.*, ix., 25).—Rose's process consists in reducing the metals in hydrogen, and dissolving out the tin with  $\text{HCl}$  (see 1350). It is difficult to reduce the  $\text{WO}_3$ , and the tin may volatilize. By igniting with  $(\text{NH}_4)\text{Cl}$  stannic acid is vapourized;  $\text{WO}_3$  remains. Repeat process to constant weight. (See 1327-29-30-56.)

1286. TALBOTT (*C. N.*, xxii., 190).—Fuse oxides with KCN. The tin is reduced to metal and filtered from alkaline tungstate dissolved in water. Mo is not similarly separated.
1287. DONATH and MÜLLNER (*J. C. S.*, liv., 531).—Oxides mixed with zinc dust, ignited, boiled with HCl, oxidized with  $\text{KClO}_3$ , and  $\text{WO}_3$  filtered off.
1288. *Phosphorus*.—KEHRMANN (*J. I. S. I.*, 1887, ii., 371).—Boil acids with NaHO;  $(\text{NH}_4)\text{Cl}$  and  $(\text{NH}_4)\text{HO}$  added, and the P precipitated with magnesia mixture. Filtrate must be evaporated four times to recover the  $\text{WO}_3$ .
1289. *Vanadium*.—FRIEDHEIM (*C. N.*, lxi., 220).—The acids are precipitated together with  $\text{HgNO}_3$  and  $\text{HgO}$ , and moist precipitate dissolved in HCl; on largely diluting, the  $\text{WO}_3$  is re-precipitated and separated by filtration.
1290. GIBBS (*J. C. S.*, xlvi., 713).—Slightly alkaline solution boiled with large quantity of  $(\text{NH}_4)\text{NO}_3$ ; metavanadate precipitated on standing. ROSENHEIM (*J. C. S.*, lvi., 762) says Gibb's process is erroneous.
1291. ROTHENBACH (*J. C. S.*, lx., 18).—The acids precipitated together with  $\text{HgNO}_3$ ; the vanadic acid determined separately by reduction and titration with  $\text{KMnO}_4$ , or by boiling with  $\text{H}_3\text{PO}_4$ , KBr, and HCl, absorbing liberated Br in KI, and titrating the free iodine.
1292. BROWNING and GOODMAN (*J. C. S.*, lxxii., 234).—Va can be estimated in the presence of both W and Mo by reducing with some organic acid, and titrating with iodine. (See also 1358.)
1293. *Titanium*.—DEFACQZ (*C. N.*, lxxiv., 293).—Heated with  $\text{KNO}_3$  and  $\text{K}_2\text{CO}_3$ ; W in water extract; precipitate as mercurous tungstate.
1294. *Gold*.—SMITH and WALLACE (*J. C. S.*, lxii., 920).—Both W and Mo are separated electrolytically.
1295. *Molybdenum*.—FRIEDHEIM and MEYER (*J. C. S.*, lxiv., 125).—Tungsten compounds always contain molybdenum; it is separated as sulphide from a solution of the metatungstate.
1296. BENNEVILLE (*J. I. S. I.*, 1895, i., 209).—Precipitated together as lead salts, heated in stream of HCl, residual tungsten determined, and Mo calculated by difference.
1297. SMITH and OBERHOLTZER (*C. N.*, lxviii., 6).—By volatilizing Mo in current of HCl. SMITH and MAAS (*C. N.*, lxviii., 207) make an atomic weight determination in this way.
1298. WADDELL (*C. N.*, lv., 101).—Add tartaric acid to prevent precipitation of  $\text{WO}_3$  on acidification; the Mo is then precipitated with  $\text{H}_2\text{S}$ .
1299. DESI (*J. C. S.*, lxxiv., ii., 221).— $\text{WO}_3$  insoluble in  $\text{H}_2\text{SO}_4$ ;  $\text{MoO}_3$  easily dissolved; hence a means of separating them.
1300. RUEGENBERG and SMITH (*C. N.*, lxxxiii., 5).—Most favourable conditions for separating as in 1299. (See also 1370.)
1301. IBBOTSON and BREARLEY (*C. N.*, lxxxi., 13).— $\text{MoO}_3$  is not easily separated by ignition (see 1329). Dissolve Pb salts in HCl, evaporate, take up in dilute HCl and filter; all the Mo in solution.

1302. *Antimony*.—HALLOPEAU (*J. C. S.*, lxxiv., ii., 540).—The metals are precipitated as mercurous antimonio-tungstate, ignited to oxides, and the antimony reduced by fusion with KCN.
1303. *Antimony, Arsenic, and Iron*.—COBENZL (*C. N.*, xlvi., 13).—Digest with aqua regia, evaporate, take up with  $\text{HNO}_3$  and tartaric acid, and filter off  $\text{WO}_3$ . (See 1357.)
1304. *Silver, Mercury, and Cadmium*.—SMITH and FRANKEL (*J. S. C. I.*, 1890, 1067).—Separated electrolytically from both W and Mo.
1305. *Chromium*.—SMITH and DIECK (*C. N.*, lxviii., 68).—Evaporate with HCl. Pure  $\text{WO}_3$  remains insoluble on again digesting with HCl. (See 1337.)
1306. *Various*.—IBBOTSON and BREARLEY (*C. N.*, lxxx., 293).—The alkalis, alkaline earths, Zn, Cd, Mn, Ni, Co, Hg, As, Ur, and Fe do not interfere with the precipitation of W as  $\text{PbWO}_4$  followed by solution in HCl, and precipitation of  $\text{WO}_3$  by diluting.

## II. Gravimetric Estimations.

1307. BERNOULLI (*C. N.*, v., 116).—Fuse insoluble tungstates with sodium carbonate; neutralize extract with acetic acid, precipitate with lead acetate, digest  $\text{PbWO}_4$  in ammonium sulphide, evaporate filtrate with  $\text{HNO}_3$ , and weigh  $\text{WO}_3$ . By treating the nearly dried nitric acid solution with ammonia, niobic acid is left undissolved.
1308. ZETTOR (*C. N.*, xvi., 12).—By precipitating with lead acetate from a faintly acetic acid solution. (See 1309.)
1309. BREARLEY (*C. N.*, lxxix., 66).—The precipitate formed in acetic solutions with lead acetate is an indefinite acid tungstate of lead containing all the W. On dissolving in strong HCl and diluting, all the  $\text{WO}_3$  is re-precipitated.  $\text{PbWO}_4$  is soluble in alkaline acetates and chlorides, but not in nitrates. True  $\text{PbWO}_4$  is formed in faintly ammoniacal solution, in presence of  $(\text{NH}_4)\text{NO}_3$ , by a few minutes' boiling.
1310. KERN (*C. N.*, xxxv., 67).— $\text{WO}_3$  and  $\text{SiO}_2$  separated from acid solution of iron, washed with HCl and alcohol.  $\text{SiO}_2$  separated with ammonia, and  $\text{WO}_3$  precipitated from caustic filtrate with HCl.
1311. PARRY and MORGAN (*C. N.*, lxvii., 260).—Acid solution of the steel is evaporated, but not baked. Filtered  $\text{SiO}_2$  and  $\text{WO}_3$  separated with ammonia. (See 1279.)
1312. M'KENNA (*C. N.*, lxxxii., 67).—Attack steel with HCl,  $\text{HNO}_3$ , evaporate, wash undissolved residue with 5 per cent.  $\text{HNO}_3$  and collect  $\text{WO}_3 + \text{SiO}_2$ . Determine S (evolution), Si, W, Mn( $\text{KClO}_3$ ), and Cr (1007) on one sample.
1313. IBBOTSON and BREARLEY (*C. N.*, lxxxii., 224).—Digest steel with HCl, just oxidize with  $\text{HNO}_3$ , boil to  $\text{WO}_3$ , precipitate, dilute, and collect  $\text{WO}_3$ . Analysis of steel-making W alloys, W powders, and W-Mo steels.



1314. AUCHY (*J. C. S.*, lxxvi., ii., 524).—The  $\text{Fe}_2\text{O}_3$  associated with  $\text{WO}_3$  obtained by evaporating acid solution of steel is fairly constant and need not be separately estimated.
1315. KEMERY (*J. I. S. I.*, 1894, i., 614).—Dissolve in nitro-sulphuric acid, evaporate to  $\text{SO}_3$  fumes, separate  $\text{SiO}_2$  with  $\text{HF}$ .
1316. SCHNEIDER and LIPP (*C. N.*, li., 297).—Steel attacked with  $\text{Br}$  and  $\text{HNO}_3$ ; evaporated; residue not soluble in dilute  $\text{HNO}_3$  fused and evaporated with  $\text{HNO}_3$ ;  $\text{SiO}_2$  and  $\text{WO}_3$  separated with  $\text{KHSO}_4$  and  $(\text{NH}_4)_2\text{CO}_3$ .
1317. VIENNA ASSAY OFFICE (*J. I. S. I.*, 1884, 230).—Decompose with aqua regia or bromine; separates  $\text{SiO}_2$  as in 1316.
1318. PERILLOU (*J. I. S. I.*, 1884, 629).—Dissolve in  $\text{HNO}_3$ , evaporate, redissolve, boil two hours, weigh  $\text{WO}_3 + \text{SiO}_2$ , and heat to redness in dried  $\text{HCl}$  gas. The tungsten is volatilized (see 1280); residual silica weighed.
1319. SCHNEIDER (*J. I. S. I.*, 1885, 245).—Iron alloys treated with  $\text{HCl}$  repeatedly. Only traces of tungsten pass into solution from rich alloys.
1320. NAMIAS (*J. C. S.*, lxii., 539).—Rich alloys digested with  $\text{Br}$  in an alkaline solution and then evaporated with  $\text{HCl}$ .  $\text{WO}_3 + \text{SiO}_2$  ignited in hydrogen (see 1285); the loss in weight being calculated to  $\text{WO}_3$ . Steel digested with  $\text{HCl}$  in absence of air; what little passes into solution is recovered by evaporating with sugar; charred residue contains  $\text{WO}_3 + \text{SiO}_2$ .
1321. PREUSSER (*C. N.*, lx., 37).—In rich alloys, powdered sample ignited to  $\text{WO}_3$ , evaporated with acids, residue fused with sodium carbonate, extract precipitated with  $\text{HCl}$ ,  $\text{SiO}_2$  separated with ammonia,  $(\text{NH}_4)_2\text{WO}_4$  evaporated and ignited to  $\text{WO}_3$ . Notes the solubility of  $\text{SiO}_2$  in ammonia.
1322. ZIEGLER (*C. N.*, lx., 272).—Points out that tungsten attacks platinum, probably forming an alloy. Throws the  $\text{W}$  powder on to fused  $(\text{NH}_4)\text{NO}_3$ , which effects a superficial oxidation, and is volatilized.
1323. WDOWISZEWSKI (*J. I. S. I.*, 1895, ii., 597).—The  $\text{FeW}$  alloy fused with borax glass and  $\text{NaK}$  carbonates; water extract evaporated with  $\text{HCl}$ ; washing with dilute  $(\text{NH}_4)\text{NO}_3$  prevents  $\text{WO}_3$  passing through the filter.
1324. CREMER (*J. S. C. I.*, 1895, 679).—Fuse the ore with pyrosulphate ( $\text{K}_2\text{S}_2\text{O}_7$ ), dissolve in dilute  $\text{HCl}$ , add cinchonin, and wash  $\text{WO}_3$  with cinchonin solution. Separate  $\text{SiO}_2$  with ammonia.
1325. ZIEGLER (*J. I. S. I.*, 1890, i., 373).—Fuse with sodium nitrate, evaporate extract with acid, separate  $\text{SiO}_2$  and  $\text{WO}_3$  with  $\text{HF}$ . Any  $\text{W}$  in the fusion residue is separated and precipitated with  $\text{HgNO}_3$ .
1326. ZIEGLER (*J. S. C. I.*, 1890, 216).—Behaviour of reagents with metallic  $\text{W}$ . Oxidation of a sample gauged by dusting into  $\text{Na}_2\text{CO}_3$  kept fluid so that the  $\text{W}$  may sink promptly. Steel is attacked with nitro-sulphuric acid. A detailed account of process 1325. (See also *J. S. C. I.*, 1891, 388.)



1327. HELMHACKER (*J. S. C. I.*, 1896, 656) and SETLIK (*C. N.*, lxi., 54).—Wolfram ore fused with sodium carbonate;  $\text{WO}_3$  precipitated from filtrate with acids; and  $\text{SiO}_2$  and  $\text{SnO}_2$  separated with HF and KCN fusion respectively.
1328. FRITCHIE (*J. S. C. I.*, 1901, 840).—Digest ore with HCl and HF, expel HF, remove  $\text{SnO}_2$ , boil to low bulk, dilute, and collect  $\text{WO}_3$ .
1329. BULLNHEIMER (*J. I. S. I.*, 1901, i., 529).—Fuse ore with  $\text{Na}_2\text{O}_2 + \text{NaHO}$ . From soluble portion remove  $\text{SiO}_2$  and  $\text{SnO}_2$  with  $\text{AmNO}_3$  and As and P with Mg. Precipitate  $\text{WO}_3$  with  $\text{HgNO}_3$  and ignite (if Mo is present) with  $\text{AmCl}$ .
1330. BORNRÄGER (*J. S. C. I.*, 1900, 855).—Fuse ore with NaHO; 100—unattacked residue =  $\text{WO}_3$  to within 5 per cent. Evaporate filtrate with acids, separate  $\text{SiO}_2$  and  $\text{SnO}_2$  with  $\text{AmHO}$  and re-evaporate for  $\text{WO}_3$ . Sb found in metallic W; precipitation with  $\text{HgNO}_3$  not trustworthy.
1331. CARNOT and GOUTAL (*J. C. S.*, lxxii., 521).—Iron separated with copper solution. Residue freed from  $\text{SiO}_2$ , fused, and precipitated with  $\text{HgNO}_3$ .
1332. SCHÖFFEL (*C. N.*, xli., 31; and *J. I. S. I.*, 1880, 345).—Separate iron with solution of copper-ammonium chloride, and precipitate fused residue with  $\text{HgNO}_3$ .  $\text{SiO}_2$  separated by fusion with  $\text{KHSO}_4$ . Roast alloys of over 12 per cent. W, and fuse. Dissolve steels in aqua regia, dilute, and allow to stand one to two days.
1333. BAGLEY and BREARLEY (*C. N.*, lxxxii., 270).—Use Cu solutions containing 10 to 33 per cent. concentrated HCl in 1332 when the steel contains Cr. Ignite residue to  $\text{WO}_3$ , weigh and correct for  $\text{SiO}_2 \cdot \text{Fe}_2\text{O}_3$  impurities.
1334. VON DER PFORDEN (*C. N.*, l., 18).—Precipitation with  $\text{HgNO}_3$  (Berzelius's method) or evaporation with HCl.
1335. SMITH and BRADBURY (*J. C. S.*, lxii., 241).—Tungsten may be estimated by means of its Ba, Pb, or Cd salts, but not effectually by means of the Sr, Ca, Ag, Co, or Bi salts.
1336. LEFORT (*C. N.*, xlv., 57).—To slightly acetic solution of a soluble tungstate add quinine acetate or sulphate. Destroy quinine by igniting and treating with  $\text{HNO}_3$ . Method exact.
1337. M'KENNA (*J. S. C. I.*, 1893, 1185).—FeW alloys decomposed with sodium peroxide in Cu crucible;  $\text{WO}_3$  precipitated by evaporation with HCl; Cr and Al are separated by  $(\text{NH}_4)\text{HO}$ . Carbon is determined by fusing with peroxide and estimating the carbonates formed.
1338. PHILIPP (*J. S. C. I.*, 1882, 152).—Powdered tungsten bronze heated with an ammoniacal solution precipitates Ag equivalent to the oxygen needed to completely oxidize the compound. The  $\text{Na}_2\text{O}$  and  $\text{WO}_3$  are determined in the filtrate.
1339. IBBOTSON and BREARLEY (*C. N.*, lxxx., 294).—Indirect process for estimating W in metallic powders depending on the solubility of the oxidized metal in NaHO. Results nearly exact.

interfere. Silicates give slightly high results. Fe and Cr are separated at boiling point with soda-hydrate. Separation of Cr with ammonia (1355) not good.

## II. Gravimetric Estimations.

1361. CHATARD (*C. N.*, xxiv., 175).—Mo precipitated with lead acetate, ignited apart from filter, and weighed as  $\text{PbMoO}_4$ . Analogous process for tungsten frustrated by fineness of the precipitate. (See 1309.)
1362. BREARLEY (*C. N.*, lxxviii., 203).—Critical examination of Chatard's process.  $\text{PbMoO}_4$  may be ignited with the paper. Prolonged heating at high temperature causes only slight loss. Presence of excess acetic acid, lead acetate, alkaline nitrates, chlorides, or acetates, and salts of the metals Mn, Cu, Co, Ni, Zn, Mg, Hg are without influence. Schindler's volumetric process (1379) supplemented by a more delicate end-reaction.
1363. VON DER PFORDEN (*C. N.*, l., 18).—Precipitation with  $\text{HgNO}_3$  and reduction in hydrogen.
1364. JANNASCH and WASOWICZ (*C. N.*, lxvi., 6).—Similar to 1363.
1365. MOISSAN (*C. N.*, lxxii., 2).—Precipitates as mercurous molybdate, and determines as bioxide. This paper gives an account of the preparation and numerous properties of metallic Mo.
1366. BORNRÄGER (*J. S. C. I.*, 1900, 471).—Dissolve alloy in aqua regia, evaporate, digest with 50 per cent. alcohol and collect  $\text{MoO}_3$ .
1367. DOHLER (*C. N.*, lxxxii., 204).—Separate from acid solution of steel with  $\text{H}_2\text{S}$  at  $80^\circ$ ; digest with  $\text{Am}_2\text{S}$  and precipitate Mo in filtrate with  $\text{HCl}$ . Ignite in H and weigh  $\text{MoS}_2$ . Very tedious process.
1368. IBBOTSON and BREARLEY (*C. N.*, lxxxii., 269).—Pour acid solution of steel into  $\text{NaHO}$ , acidify the filtrate and precipitate  $\text{PbMoO}_4$  (1362). Deals also with influence of Mo on other estimations and analysis of Mo metal and steel-making alloys of Mo.
1369. GUICHARD (*J. C. S.*, lxxviii., ii., 370).—Decompose molybdenite with  $\text{HNO}_3$ , or by fusion and estimate as  $\text{PbMoO}_4$ . Or, heat in O and collect sublimed  $\text{MoO}_3$ .
1370. SMITH and BRADBURY (*J. C. S.*, lxii., 241).—Same available precipitants as for W (see 1335). Suggest the estimation of W and Mo together as Cd salts and electro-estimation of Cd in another portion as a means of determining W and Mo in mixtures.
1371. PECHARD (*C. N.*, lxxv., 89).—Volatilized in  $\text{HCl}$  gas as  $\text{MoO}_3 \cdot 2\text{HCl}$ . The compound is dissolved in water, evaporated, and  $\text{MoO}_3$  weighed. Tungstates are not at all volatilized, and may be thus separated (1296 and 1297).
1372. SMITH and HOSKINSON (*C. N.*, liii., 278).—Deposited electrolytically from acid solution of the molybdates as  $\text{Mo}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  and so weighed, or ignited to  $\text{MoO}_3$ . See also KOLLOCK and SMITH (*J. C. S.*, lxxx., ii., 694).

1373. HEIDENREICH (*J. S. C. I.*, 1896, 744).— $\text{Mo}_2\text{O}_3$  is not completely deposited from solution of  $(\text{NH}_4)_2\text{MoO}_4$  in four days.
1374. FREIDHEIM and EULER (*J. C. S.*, lxxviii., 535). Precipitated as sulphide, filtered, ignited short of losing Mo, digested with  $(\text{NH}_4)\text{HO}$ , evaporated, and ignited to  $\text{MoO}_3$ .
1375. TAGGART and SMITH (*J. C. S.*, lxxii., 433).—Mo sulphide ignited with oxalic acid burns to pure  $\text{MoO}_3$ .

### III. Volumetric Estimations.

(See also 891, etc.)

1376. WERNCKE (*C. N.*, xxxii., 259).—In Pisani's process (reduction with Zn and titration with permanganate) the reduction is not to the sesquioxide. Sodium amalgam does not effect a complete reduction. The results are mutually comparable.
1377. BENNEVILLE (*J. I. S. I.*, 1895, i., 228).—Pisani's process. The temperature at which the reduction is made has no influence on results; nitric acid must be absent; H boiled off before titrating.
1378. VON DER PFORDEN (*C. N.*, l., 18).—HCl solution reduced and titrated in presence of  $\text{H}_2\text{SO}_4$  and  $\text{MnSO}_4$ . Similar process for W; the reduced solution (red) added to excess permanganate; excess estimated with  $\text{FeSO}_4$ .
1379. SCHINDLER (*C. N.*, lviii., 61).—Faintly acetic solution precipitated with standard lead acetate, using tannin as indicator. Lead may be estimated inversely. (See 1362.)
1380. SEUBERT and POLLARD (*C. N.*, lxxii., 293).— $\text{MoO}_3$  is dissolved in standard soda and excess titrated with HCl and phenolphthalein.
1381. FRIEDHEIM (*C. N.*, lxxv., 91).—Molybdate decomposed with KI and HCl; iodine absorbed and titrated with thiosulphate. A discussion of modified process by Gooch and Fairbanks. Gooch defends his modifications (*C. N.*, lxxv., 208; and *C. N.*, lxxviii., 207).
1382. FRIEDHEIM and EULER (*J. C. S.*, lxxviii., 535).—By distilling first with HCl and HBr, and then with HCl, KI, and phosphoric acid, both V and Mo are estimated from the Br and I liberated.

### IV. Detection and Miscellaneous Notes.

1383. SCHLOSBERGER (*C. N.*, iii., 192 and 204).—Dilute solution of  $(\text{NH}_4)_2\text{MoO}_4$  gives blue colour with a soluble sulphide.
1384. SKEY (*C. N.*, xvi., 324).—An HCl solution shaken with zinc gives a red colour, which detects one part in two millions. Fe does not interfere if time be allowed it to deoxidize. W gives a like colour. (See also ELBRAM, *J. C. S.*, lxxii., 522.)
1385. MOISSAN (*C. N.*, lxxii., 2).—Heated with phosphorus perchloride, reddish fumes condense in a ring.

1386. SCHONN (*C. N.*, xxi., 166).—Heated with  $\text{H}_2\text{SO}_4$  a blue colour appears. MASCHKE (*C. N.*, xxxviii., 22) describes a more convenient and certain modification of the test.
1387. SMITH (*J. C. S.*, lxiv., 171).—Mo precipitates Ag from ammoniacal AgCl quantitatively; similarly from solutions of auric chloride; tungsten acts in a similar way; Mo and W (less readily) reduce HgCl,  $\text{MoO}_2$  also precipitates Ag. (See SMITH and SHINN, *C. N.*, lxx., 197; also 1338.)
1388. MONTEMARTINI (*J. C. S.*, lxii., 1402).—Strong  $\text{HNO}_3$  attacks Mo slowly; more dilute acids do not at once convert what they dissolve into  $\text{MoO}_3$ .
1389. GUICHARD (*J. C. S.*, lxxii., 496).—Mo alone is formed on igniting  $\text{MoO}_3$  in hydrogen at  $600^\circ \text{C}$ .
1390. IGELSTRÖM (*J. C. S.*, lxviii., ii., 505).—In Swedish hæmatite  $\text{Mo}_2\text{O}_3$  was found up to 9 per cent.

## VANADIUM.

The arrangement is :

- I. SEPARATION FROM OTHER ELEMENTS.
- II. GRAVIMETRIC ESTIMATIONS.
- III. VOLUMETRIC ESTIMATIONS.
- IV. DETECTION.
- V. MISCELLANEOUS NOTES.

### I. Separation from other Elements.

*Iron (or Al):*

1391. BETTENDORF (*C. N.*, xxxvii., 113).— $\text{AmHO}$  precipitates vanadate of Al, which is decomposed by  $\text{Am}_3\text{PO}_4$ , the V passing into solution. The reaction with ferric salts is similar.
1392. CARNOT (*C. N.*, lvi., 16).—Fe is separated by repeated precipitations with  $\text{AmHO}$ , acetate, or  $\text{H}_2\text{S}$ ; not so Cr or Al.
1393. BAMBER (Process 958).—Separates V and Fe. (See also 1427.)
1394. HELOUIS (*J. S. C. I.*, 1896, 657).—From Al-V alloys the Al is dissolved by HCl. The residual V is not attacked by HCl or alkalis. Influence of V on physical properties of irons.

*Chromium :*

1395. CLASSEN (*J. C. S.*, l., 428).—Fuse the mixed oxides with  $\text{Na}_2\text{CO}_3$  and S; the Cr remains as oxide. Analytical characters of insoluble V compounds of Pb, Ba, and  $\text{NH}_3$  given.

1396. KLECKI (*C. N.*, lxi., 54).—The V is precipitated from acetic solution with Ur; the chromate is easily soluble.
- 1396a. HILLEBRAND (*C. N.*, lxxxiii., 212).—Separates W, Mo, Cr, As, and P from V by digesting Pb salts with strong  $K_2CO_3$  solution.

*Arsenic:*

1397. FIELD and SMITH (*C. N.*, lxxv., 26).—Heat the mixed sulphides below  $250^\circ$  in HCl gas; As volatilized. As oxides, both metals volatilize, and are thus separated from vanadinite.
1398. FRIEDHEIM and MICHAELIS (*J. C. S.*, lxxviii., ii., 415).—Eliminate As by distilling with methyl alcohol and HCl, after adding  $SO_2$  to form  $V_2O_4$ . (See also 1412.)
1399. *Titanium*.—DEVILLE (*C. N.*, iii., 226).—Fuse rutile with  $KHO + KNO_3$ , leach, filter, pass  $H_2S$ , and drive  $H_2S$  from acidified filtrate; V is precipitated. Used (*C. N.*, v., 86) for estimating V in cryolite.
1400. *Sulphur*.—GOYDER (*J. C. S.*, lxxvii., 1096).—Reduce to  $V_2O_4$  with  $KNO_2$  or alcohol before adding  $BaCl_2$ , otherwise vanadic compounds are also precipitated.
1402. *Uranium*.—LALLEMAND (*C. N.*, xliii., 72).—The filtered nitric acid solution of pitchblende is precipitated with  $Na_2CO_3$ . Ur in solution; Fe, V, W, etc., precipitated. (See 1427.)
1403. *Zinc*.—HALBERSTADT (*C. N.*, xlvi., 101).—Evaporate HCl solution, digest with Am oxalate, and boil with acetic acid. V is dissolved; Zn, Ba, Ca, and Pb are precipitated.
1404. *Gallium*.—BOISBAUDRAN (*C. N.*, xlviii., 86).—From HCl solution mixed with  $As_2O_3$  and Am acetate, Ga is precipitated by  $H_2S$ ; or mix neutral solution with  $Am_2S$ , and precipitate V with HCl.

## II. Gravimetric Estimation of Vanadium.

1405. PHIPSON (*C. N.*, vii., 210).—Fuse clay ironstone with  $KNO_3$ , add KHO to filtrate, then  $H_2S$ , and precipitate sulpho-vanadate with  $HNO_3$  and  $BaCl_2$ . Decompose precipitate with  $H_2SO_4$ , and precipitate as ammonium salt. Some French processes described.  $TiO_2$  interferes with the microcosmic blowpipe test (1437).
1406. RILEY (*C. N.*, viii., 261 and 277).—When solution of iron is evaporated, V accompanies Ti and Si. V is precipitated with Fe on adding AmHO. On boiling  $KHSO_4$  fusion, V is precipitated with the basic sulphate. Dissolve Fe in HCl, wash residue with KHO, and burn off C; the final residue nearly pure V oxides.
1407. CLASSEN (*C. N.*, lv., 74).—Digest magnetite with  $H_2SO_4$ , drive off  $SO_3$ , fuse with  $Na_2CO_3 + S$ , precipitate as sulpho-vanadate by acidifying, and weigh as  $V_2O_5$ ; Cr remains insoluble.

1408. GERLAND (*C. N.*, xxxvi., 29).—V precipitated with AmCl, carries down K but not Na salts.
1409. POPE (*J. I. S. I.*, 1899, ii., 489).—Fuse ore with  $\text{NaNO}_3$ , precipitate with Ba, dissolve in  $\text{H}_2\text{SO}_4$ , convert to  $\text{AmVO}_3$ , and ignite to  $\text{V}_2\text{O}_5$ .
1410. DITTE (*C. N.*, lv., 203).—Precautions in precipitating, washing, and igniting  $\text{AmVO}_3$  so as to avoid loss through solubility, volatility, etc.
1411. BOETTGER (*C. N.*, xxix., 62).—Heat ore with nitre and soda, leach, nearly neutralize with  $\text{HNO}_3$ , and precipitate V with  $\text{Ba}(\text{NO}_3)_2$ .
1412. CARNOT (*C. N.*, lvi., 35).—V is completely precipitated from alkaline solutions as dibarium vanadate, and may be thus ignited. P, As, and partially W and Mo, are precipitated free from V by substituting Sr for Ba.
1413. GERLAND (*C. N.*, xxxvi., 271).—V is almost quite precipitated with  $\text{PbA}_2$ . Decompose precipitate with  $\text{HNO}_3$ , add  $\text{H}_2\text{SO}_4$ , and ignite evaporated filtrate to  $\text{V}_2\text{O}_5$  (readily reduced by dust and flame gases).
1414. CARNOT (*C. N.*, lvi., 42).— $\text{Hg}'$ ,  $\text{Hg}''$ , Pb, and Bi solutions all completely precipitate V from neutral or faintly alkaline solution. Precipitates can also be formed with Co, Ni, Zn, Cd, and Cu.
1415. CARNOT (*C. N.*, lvi., 16).—V precipitated with uranium nitrate is free from alkaline earths, Zn, Mn, Cu, etc. P, As, W, and Mo interfere. The ignited precipitate contains 24.22 per cent. V. MnO solutions also precipitate V quantitatively; Mo does not interfere.
1416. ROSENHEIM and FRIEDHEIM (*C. N.*, lxvi., 27).—Difficulties of estimating V in the presence of As, P, Mo, and W. Weighs the  $\text{CO}_2$  evolved in the reaction.  $\text{V}_2\text{O}_5 + \text{H}_2\text{C}_2\text{O}_4 = \text{V}_2\text{O}_4 + \text{H}_2\text{O} + 2\text{CO}_2$ . Above elements do not interfere.

### III. Volumetric Estimation of Vanadium.

1417. GENTH (*C. N.*, xxxiv., 79).—Reduce to  $\text{V}_2\text{O}_4$  with  $\text{SO}_2$ ; oxidize to  $\text{V}_2\text{O}_5$  with permanganate. Excess of  $\text{H}_2\text{SO}_4$  without influence.
1418. GERLAND (*C. N.*, xxxvi., 272).—As 1417. The first appearance of the pink colour is the final point.  $\text{KMnO}_4$  can be repeatedly standardized by pure V compounds.
1419. OSMOND and WITZ (*C. N.*, xlvii., 12).—Slag decomposed with  $\text{H}_2\text{SO}_4$ , permanganate added to faint colour, and then standard  $\text{FeSO}_4$ , using ferri-cyanide indicator. Excess  $\text{H}_2\text{SO}_4$  should be considerable. Also by comparing colour of hypovanadic solutions.
1420. DITTE, CARNOT, etc. (*C. N.*, lxviii., 77, 89, etc.).—Separation of Ba and Sr from Va. Process 1417 is not affected by Mg, Ca, or (with modification) W. Analysis of vanadio-tungstates. (See also 1289 to 1292.)
1421. ROSENHEIM (*J. S. C. I.*, 1891, 164).—The titration of  $\text{V}_2\text{O}_4$  with  $\text{KMnO}_4$  is obscured by a violet colouration when  $\text{WO}_3$  is present.

1422. L'HOTE (*C. N.*, lv., 191).—The ore mixed with C is heated with Cl. Vanadyl chloride is condensed and titrated with  $\text{KMnO}_4$  in hot solution after reducing with zinc. (See 1446.)
1423. STEAD (*J. I. S. I.*, 1893, i., 164).—In the presence of  $\text{CrO}_3$ , titrate with  $\text{FeSO}_4$  and  $\text{KMnO}_4$ , which gives V + Cr, and then with  $\text{FeSO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ , which gives V only.  $\text{V}_2\text{O}_4$  is not oxidized by  $\text{K}_2\text{Cr}_2\text{O}_7$ .
1424. RIDSDALE (*J. S. C. I.*, 1888, 73).—V in slags estimated by modification of 1419. Separation of various constituents of slag, and relative tendency of precipitates to carry down  $\text{V}_2\text{O}_5$ .
1425. JONET (*J. S. C. I.*, 1901, 620).—Fuse slag, boil nearly acidified water extract, remove  $\text{Al}_2\text{O}_3 + \text{SiO}_2$  and precipitate V with  $\text{BaNO}_3$ . Digest with  $\text{H}_2\text{SO}_4$ , re-precipitate as  $\text{AmVO}_3$ , ignite and check weight of  $\text{V}_2\text{O}_5$  by titration with  $\text{KMnO}_4$ .
1426. HILLEBRAND (*C. N.*, lxxviii., 217 and 295).—Neither  $\text{Cr}_2\text{O}_3$  nor  $\text{H}_3\text{PO}_4$  affect process 1417; Mo and As do. Describes  $\text{H}_2\text{O}_2$  test.
1427. FRITCHLE (*C. N.*, lxxxii., 258).—Fe and Ur are precipitated free from V by  $\text{Na}_2\text{CO}_3 + \text{NaHO}$ . The V in carnotite is found indirectly by estimating the Ur, the Fe + V, and then Fe + Ur + V by permanganate.
1428. HOLVERSCHEIT (*J. C. S.*, lviii., 1343).—The precipitated Ba or Pb salt is boiled with HCl and KBr. The liberated Br is estimated iodometrically.
1429. BROWNING (*C. N.*, lxx., 205).—Reduce to  $\text{V}_2\text{O}_4$  with tartaric acid, alkalize with  $\text{NaHCO}_3$ , add excess of iodine, and titrate with  $\text{As}_2\text{O}_3$ .
1430. BROWNING and GOODMAN (*J. C. S.*, lxxii., ii., 234).—Above process interfered with by Mo (not W) unless the reduction with tartaric acid is effected slowly in the cold.
1431. BROWNING (*C. N.*, lxxiv., 203).—Reduce acid  $\text{V}_2\text{O}_5$  solution with HI or HBr, and titrate as 1429.
1432. FRIEDHEIM (*C. N.*, lxxv., 125).—In 1431 it is better to collect the liberated halogen and estimate as 1428. In the presence of syrupy  $\text{H}_3\text{PO}_4$ , the reduction may be carried to  $\text{V}_2\text{O}_3$ .
1433. KLECKI (*J. C. S.*, lxvi., ii., 162).—Dextrose added to a sulphuric solution of V in the presence of Fe gives a green colouration from which the V may be approximately deduced.
1434. MAILLARD (*C. N.*, lxxxii., 19).—Ether saturated with  $\text{H}_2\text{O}_2$  is added and the colour compared with standards. Heavy metals may be removed by  $\text{H}_2\text{S}$  or  $\text{Am}_2\text{S}$ , and soluble alkaline salts do not interfere.

#### IV. Detection of Vanadium.

1435. DEVILLE (*C. N.*, iv., 241).—The sulphovanadite formed on passing  $\text{H}_2\text{S}$  through an alkaline solution is a very delicate test for V. In *C. N.*, v., 103, it is used for approximately estimating V in cast-iron.
1436. APJOHN (*C. N.*, xxvi., 183).—Fuse mineral with  $\text{Na}_2\text{CO}_3$ , remove  $\text{SiO}_2$  and metals precipitable with  $\text{H}_2\text{S}$ , and apply 1435.

1437. DEVILLE (*C. N.*, v., 86).—Tested with P salt, V gives intense green in the R. F., yellow in the O. F. (See 1405.)
1438. SONSTADT (*C. N.* xxvi., 215).—If strong  $\text{KIO}_3$  be added to sea-water, V can be detected in the precipitate by blowpipe reactions.
1439. GUYARD (*C. N.*, xxxiii., 71).—Add salt of aniline and a chlorate to HCl solution ; rapid formation of aniline-black = V.
1440. WITZ and OSMOND (*C. N.*, liii., 252).—Soak prepared calico strips in solution to be tested, and compare with standard strips after treating with aniline-black mixture minus the hypovanadate.
1441. HAYES (*C. N.*, xxxi., 167).—Gall forms a greenish black precipitate in acid V solutions. In the presence of  $\text{MnO}$ ,  $\text{AmHO}$  gives a blue solution, like Cu.
1442. SMITH (*C. N.*, lxi., 20).—Add dilute ferro-cyanide to  $\text{H}_2\text{SO}_4$  solution ; a green colour = V. Both  $\text{NaHO}$  and  $\text{KHO}$  may contain V.
1443. ELBRAM (*J. C. S.*, lxxii., ii., 522).—Faintly acid solution of  $\text{KCNS}$  gives a yellow colour ; more strongly acid, a blue colour with V.
1444. LEVY (*J. C. S.*, lii., 305).—The dark green colour given by  $\text{V}_2\text{O}_5$  with resorcinol distinguishes it from  $\text{MoO}_3$  or  $\text{P}_2\text{O}_5$ .
1445. STEAD (*J. I. S. I.*, 1893, i., 170).—V is always present in British chromiferous pig-irons. Detects with  $\text{H}_2\text{O}_2$ .

#### V. Miscellaneous Notes.

1446. ROSCOE (*C. N.*, xvii., 135).—In acid solution, zinc forms  $\text{V}_2\text{O}_2$  ; magnesium,  $\text{V}_2\text{O}_3$  ; and  $\text{SO}_2$  or  $\text{H}_2\text{S}$  form  $\text{V}_2\text{O}_4$ . The relation of V to N, P, As, Sb, etc.
1447. ROSCOE (*C. N.*, xx., 37).—V is insoluble in HCl, soluble in  $\text{H}_2\text{SO}_4 + \text{HF}$  or  $\text{HNO}_3$ , and fused with formation of vanadates.
1448. GENTH and VOM RATH (*C. N.*, liii., 218).—Outline of process for analysis of V minerals containing Pb, Cu, Zn, Mn, Fe, As, P, etc.
1449. PROCTER-SMITH (*J. S. C. I.*, 1901, 1183).—Preparation of Fe-V alloys ; effect of V on steel, and estimation of V in ores ; alloys and steel by fusion, separation, and  $\text{KMnO}_4$  titration.
1450. HINTZ and WEBER (*C. N.*, lxx., 157).—How to precipitate V with  $\text{AmCl}$  ; precipitation with Ba in the presence of alkaline salts ; and the main portions of 1415 and 1420.
1451. COWPER-COLES (*C. N.*, lxxix., 147).—Electro-deposition of V. Some chemical properties and commercial uses.
1452. READ (*J. C. S.*, lxxv., 31)<sub>yp</sub>—At high temperatures  $\text{V}_2\text{O}_5$  gives off O. It readily re-oxidizes on cooling.  $\text{V}_2\text{O}_4$  crystals may be thus obtained.
1453. WITZ and OSMOND (*J. I. S. I.*, 1882, 770).—V concentrates in (notably the Thomas-Gilchrist) slags.



**TITANIUM.**

The arrangement is :

- I. SEPARATION FROM OTHER ELEMENTS.
- II. GRAVIMETRIC ESTIMATION.
- III. VOLUMETRIC ESTIMATION.
- IV. DETECTION.
- V. MISCELLANEOUS NOTES.

**I. Separation from other Elements.**

*Iron.* (See also 1758, 1767.)

- 1454. STREIT and FRANZ (*C. N.*, xxi., 120).—Ti is precipitated by boiling the  $\text{H}_2\text{SO}_4$  solution, containing considerable acetic acid, free from Fe or Zr.
- 1455. BASKERVILLE (*J. C. S.*, lxvi., ii., 401).—The separation by boiling is more easy and accurate when the metals exist as chlorides.
- 1456. DEVILLE (*C. N.*, v., 102).—To  $\text{H}_2\text{SO}_4$  solution add AmHO, evaporate the whole to dryness, and dissolve out Fe and Al with dilute  $\text{HNO}_3$ ; the residual Ti is calcined and weighed.
- 1457. WALKER (*J. C. S.*, lxxiv., ii., 540).—The Fe is repeatedly precipitated with ammoniacal  $\text{H}_2\text{O}_2$ ; Ti in the filtrates.
- 1458. *Aluminium.*—GOOCH (*C. N.*, lii., 55, etc.).—Separation with NaHO or by boiling acid solution inexact. Separate with AmHO and acetic acid or microcosmic salt and formic acid. Fe is precipitated by  $\text{H}_2\text{S}$  from alkaline tartrate solutions.

*Tin.*

- 1459. ROSE (*C. N.*, v. 87).—Fuse oxides with soda and sulphur. The Sn is dissolved out with water.
- 1460. HILGAR and HAAS (*C. N.*, lxi., 209).—Reduce the mixed oxides in H; dissolve out Sn with HCl. Silicates are decomposed with  $\text{H}_2\text{SO}_4 + \text{HF}$ . (See also HAAS, *J. C. S.*, lviii., 1029.)
- 1461. *Silica.*—HOLLAND (*C. N.*, lix., 27).—If  $\text{H}_2\text{SO}_4$  be not present, Ti is volatilized on treating with HF. Even after two precipitations,  $\text{TiO}_2$  contains Fe.  $\text{TiO}_2$  dissolves in HCl if  $\text{Al}_2\text{O}_3$  is also present. A scheme for the analysis of Ti silicates. (See also 210 and 219.)
- 1462. *Niobium.*—MARIGNAC (*C. N.*, xvii., 119 and 121).—Fuse the acids with fluorhydride, reduce HCl solution of the melt with zinc, and titrate (Ti only) with  $\text{KMnO}_4$  (see 1488). DEMARÇAY (*J. C. S.*, xlviii., 639) treats the HF solution of the oxides (including Zr) with KHO short of alkalinity; the Ti remains in solution.
- 1463. *Gallium.*—BOISBAUDRAN (*C. N.*, xlvi., 164).—Precipitate Ti with KHO from boiling solution. Four other methods given.

**II. Gravimetric Estimation of Titanium.**

1464. SCHEERER (*C. N.*, i., 143).—Decompose silicate as usual, vaporize  $\text{SiO}_2$  with  $\text{HF}$ , and add the residue to precipitate formed in the filtrate with  $\text{AmHO}$ . Fuse with  $\text{KHSO}_4$ , reduce  $\text{Fe}$  with  $\text{H}_2\text{S}$ , and precipitate  $\text{TiO}_2$  by boiling.
1465. TOSH (*C. N.*, xvi., 168).—Solution and residue treated as 1464. Precipitate  $\text{Fe}$  and  $\text{Ti}$  from solution of  $\text{KHSO}_4$  fusion with  $\text{AmHO}$ , dissolve out  $\text{Fe}$  with  $\text{Am}_2\text{S}$  and  $\text{SO}_2$ , and weigh residual  $\text{TiO}_2$ ; results approximate.
1466. FORBES (*C. N.*, xviii., 275).—Fuse ore with  $\text{KHSO}_4$ , separate  $\text{SiO}_2$ , and precipitate  $\text{TiO}_2$  by boiling much diluted filtrate after acidifying with  $\text{HNO}_3$ .
1467. BETTEL (*C. N.*, xxviii., 93).—As 1466; but omits  $\text{HNO}_3$ , and adds  $\text{SO}_2$  before boiling.
1468. FORBES (*C. N.*, xix., 3).—Decompose powdered mineral with  $\text{H}_2\text{SO}_4$  or  $\text{NaHSO}_4$ , and proceed as before. The  $\text{Ti}$ , which goes into solution on dissolving  $\text{Fe}$  in aqua regia, is all contained in a small precipitate formed with  $\text{AmHO}$ .
1469. ROUSSEL (*C. N.*, xxviii., 313).—Decompose the mineral with soda. Separate  $\text{TiO}_2$  and  $\text{SiO}_2$  with concentrated  $\text{H}_2\text{SO}_4$ ;  $\text{Ti}$  from the filtrate with  $\text{SO}_2$ , etc., and from co-precipitated  $\text{Al}_2\text{O}_3$  by digesting with  $\text{HCl}$ . (See 1461.)
1470. ANON. (*J. I. S. I.*, 1895, i., 514).—Reduce ore in  $\text{H}$ , dissolve in  $\text{HCl}$ , fuse residue, dissolve insoluble titanate in  $\text{HCl}$ , precipitate  $\text{Fe}$  and  $\text{Al}$  from tartrate solutions with  $\text{H}_2\text{S}$ , and precipitate  $\text{TiO}_2$  by boiling with glacial acetic acid.
1471. LEDEBUR (*J. I. S. I.*, 1885, 300).—Dissolve ore in  $\text{HCl}$ , re-treating the insoluble portion; evaporate filtrate with  $\text{H}_2\text{SO}_4$ , partially neutralize, and precipitate by boiling with  $\text{SO}_2$ .  $\text{HNO}_3$  solution of iron evaporated and treated as ore.
1472. PARRY and MORGAN (*C. N.*, lxvii., 260).—Decompose pig-iron with  $\text{HCl}$ , fuse ignited residue with  $\text{KHSO}_4$ , and precipitate  $\text{Ti}$  by boiling. Describe also Riley's process, in which  $\text{Ti}$  is carried down by a little basic ferric acetate.
1473. CLASSEN (*J. C. S.*, liv., 532).—Precipitate  $\text{Fe}$  with  $\text{KHO} + \text{H}_2\text{O}_2$  (see 1457), filter, boil off  $\text{H}_2\text{O}_2$ , and precipitate  $\text{Ti}$  with  $\text{AmHO}$ . Any  $\text{Ti}$  carried down with the iron remains suspended when the oxalate solution of the latter is electrolyzed.
1474. BRAKES (*J. S. C. I.*, 1899, 1097).—Dissolve ore and fusion of the residue in  $\text{HCl}$ , nearly neutralize, boil with  $\text{SO}_2$ , remove  $\text{SiO}_2$  with  $\text{HF}$ , and weigh  $\text{TiO}_2$ .
1475. BASKERVILLE (*J. S. C. I.*, 1900, 419).—Fuse ore with  $\text{NaF} + \text{KHSO}_4$ , neutralize  $\text{HNO}_3$  solution of the melt, and from faintly  $\text{HCl}$  solution precipitate  $\text{TiO}_2$  by boiling. The estimation of  $\text{Si}$ ,  $\text{S}$ ,  $\text{P}$ , etc., described.

1476. HUNT, CLAPP, and HANDY (*C. N.*, lxxv., 235).—Decompose Al-Ti alloy with KHO, fuse residue of Fe and Ti with KHSO<sub>4</sub>, and precipitate TiO<sub>2</sub> by boiling.
1477. ZIEGLER (*C. N.*, lxxvi., 321).—Fe-Ti alloy fused with NaHSO<sub>4</sub>, SiO<sub>2</sub> eliminated, and TiO<sub>2</sub> precipitated by boiling. H<sub>2</sub>SO<sub>4</sub> driven from the precipitate by igniting with Am<sub>2</sub>CO<sub>3</sub>.
1478. JENNINGS (*J. I. S. I.*, 1888, 331).—Decompose ore with HCl, boil with SO<sub>2</sub> and acetic, fuse precipitate and residue, dissolve sodium titanate in H<sub>2</sub>SO<sub>4</sub>, and re-precipitate by boiling. (See also VOGT, *J. I. S. I.*, 1901, i., 528.)
1479. AUSTEN and WILLBUR (*C. N.*, xlvi., 113).—TiO<sub>2</sub> can be precipitated from HCl solution of FeO as well as by the usual method if acetic acid be added.
1480. MORGAN (*C. N.*, lxxv., 134).—Evaporate acid solution of iron with H<sub>3</sub>PO<sub>4</sub>, fuse insoluble phospho-titanate successively with K<sub>2</sub>CO<sub>3</sub> and KHSO<sub>4</sub>, and precipitate TiO<sub>2</sub> with acetate.
1481. LEVY (*C. N.*, lvi., 209).—The liquid should contain exactly 0.5 per cent. free H<sub>2</sub>SO<sub>4</sub>, and then be boiled for six hours. Zn, Cu, Mg, Al, no effect; Fe makes results high.
1482. APJOHN (*C. N.*, xxvi., 183).—Decompose rock with KHSO<sub>4</sub>, precipitate Ti by boiling, and weigh as titano-fluoride of potassium.
1483. DROWN and SHIMER (*C. N.*, xlii., 299).—Heat iron in Cl, absorb Si and Ti in water, evaporate with HCl and H<sub>2</sub>SO<sub>4</sub> to separate SiO<sub>2</sub>, and precipitate Ti by boiling. Results higher than Riley's process (1472).
1484. SHIMER (*C. N.*, lv., 156).—Agreeing determinations of Ti in pig-iron were made—(1) By fusing HCl residue with KHSO<sub>4</sub>; (2) by dissolving Ti from residue with HNO<sub>3</sub> (see 163), and by 1483. The precipitate formed by boiling always contains P; it is separated by fusion with soda.
1485. CARNOT and GOUTAL (*J. C. S.*, lxxii., ii., 521).—Decompose Fe with neutral cupro-potassic chloride, fuse residue with KHSO<sub>4</sub>, and precipitate TiO<sub>2</sub> with SO<sub>2</sub> and acetate.
1486. MOISSAN (*C. N.*, lxxi., 103).—Ti is decomposed by KNO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>, and precipitated with AmHO. Some properties of the metal.
1487. PENNINGTON (*C. N.*, lxxv., 31).—Na<sub>2</sub>HPO<sub>4</sub> completely precipitates Ti from its double fluoride solution.

### III. Volumetric Estimation of Titanium.

1488. PISANI (*C. N.*, x., 218).—Reduce HCl solution with Zn, and titrate with KMnO<sub>4</sub>; Zr does not interfere. By using KCNS test, Ti can be titrated in presence of iron, since Ti is first oxidized. H<sub>2</sub>S and SO<sub>2</sub> do not reduce Ti. WIEGAND (*J. S. C. I.*, 1883, 363).—The estimation in the presence of Fe is unreliable.
1489. WELLS and MITCHELL (*C. N.*, lxxiii., 123).—Decompose ore with acids and KHSO<sub>4</sub>, reduce, and titrate H<sub>2</sub>SO<sub>4</sub> solution (even in the presence of iron) as 1488.

1490. WELLER (*J. S. C. I.*, 1882, 506 and 508).—Mo, V (see 1434), and Cr interfere with the  $\text{H}_2\text{O}_2$  colour estimation of Ti;  $\text{NH}_3$  and K salts, and excesses of the reagents do not appreciably. The yellow colour is due to a higher oxide,  $\text{TiO}_3$ . (Also CLASSEN, *J. S. C. I.*, 1888, 344).
1491. DUNNINGTON (*C. N.*, lxxv., 65).—Evaporate powdered rock with HF, fuse with  $\text{KHSO}_4$ , extract with  $\text{H}_2\text{SO}_4$ , and apply 1490.
1492. DUNNINGTON (*C. N.*, lxxiv., 302).—The  $\text{KHSO}_4$  fusion should be taken up with 5 per cent  $\text{H}_2\text{SO}_4$  to prevent the formation of meta-titanic acid, which gives no colour with  $\text{H}_2\text{O}_2$ .
1493. WELLS (*J. I. S. I.*, 1886, 399).—Dissolve Fe in nitro-sulphuric acid, evaporate to  $\text{SO}_3$ , dilute, add  $\text{H}_2\text{O}_2$ , and compare with standard. Will estimate 0.01 per cent. Ti.
1494. NOYES (*J. S. C. I.*, 1891, 485).—Open up ore with  $\text{KHSO}_4$  and NaF, and apply 1490. Very small amounts of Fe interfere, but may be allowed for. (See also BRAKES, *J. S. C. I.*, 1901, 23.)
1495. HILLEBRAND (*C. N.*, lxxxiii., 177).—Particulars of  $\text{H}_2\text{O}_2$  colour estimation of  $\text{TiO}_2$  in rocks; and (p. 184) a description of some gravimetric methods.

#### IV. Detection of Titanium.

1496. RILEY (*C. N.*, iv., 84).—Treat  $\text{SiO}_2$  with HF, fuse residue with Zn and microcosmic salt in order to detect Ti in pig-iron.
1497. DEVILLE (*C. N.*, iv., 241).—Titanate of K in HCl gives with Zn a violet-blue colour. The precipitate formed with  $\text{AmHO}$  in HCl solution gives a deeper colour when heated with Sn in R.F.
1498. JACKSON (*C. N.*, xlvii., 157).—Yellow colour with  $\text{H}_2\text{O}_2$  in HCl or  $\text{H}_2\text{SO}_4$  solution; easily detects 1 part in 50,000.
1499. HILLEBRAND (*C. N.*, lxxii., 158).—HF interferes with  $\text{H}_2\text{O}_2$  test.  $\text{H}_2\text{O}_2$  may contain HF.
1500. FRESSENIUS (*C. N.*, lii., 104).— $\text{H}_2\text{SO}_3$ , which has been momentarily in contact with Zn produces an orange-red colour; about as sensitive as the  $\text{H}_2\text{O}_2$  test.
1501. LEVY (*C. N.*, liv., 301).—Moisten with  $\text{H}_2\text{SO}_4$ , and add morphine; a crimson colour = Ti.
1502. LUDEKING (*C. N.*, lxxiii., 24).—Fuse in bead of  $\text{Na}_2\text{CO}_3$  and heat in R.F.; red (cyano-nitride) colour = Ti.

#### V. Miscellaneous.

1503. RILEY (*C. N.*, i., 159).—Analysis of New Zealand iron sands. Ti determined by difference.
1504. MUSHET (*C. N.*, i., 231 and 276).—Contention that the "body" and general excellence of certain steels is due to Ti.
1505. RILEY (*C. N.*, viii., 224, etc.).—Two or three not very satisfactory processes for estimating Ti. (See 1472.)

1506. JONES (*C. N.*, lxxv., 8).—Refractory Ti minerals containing Al, Mg, Cr, etc., are decomposed by heating with  $\text{H}_2\text{SO}_4$  in sealed tube.
1507. BLONDEL (*C. N.*, lxxix., 305).—Beyond  $200^\circ$ ,  $\text{H}_2\text{SO}_4$  solutions of  $\text{TiO}_2$  deposit crystals which stop the decomposition of the mineral.  $\text{TiO}_2$  slowly precipitated at ordinary temperatures.
1508. HOGG (*C. N.*, lxxviii., 163).—As isolated crystals of cyano-nitride Ti exists in ferro-manganese.
1509. HILLEBRAND (*C. N.*, lxxviii., 94).—Description of  $\text{H}_2\text{O}_2$  colour test. Zr prevents precipitation of  $\text{TiO}_2$  by boiling acetic solutions. Separates Fe and Al from Ti as 1455.
1510. NAU (*J. I. S. I.*, 1892, ii., 437).—Ti may not be detectable in pig-iron even when the slag contains 8 per cent. or more  $\text{TiO}_2$ .
1511. REINHARDT (*J. S. C. I.*, 1888, 326).—Separation of cyano-nitride ( $\text{Ti}_5\overline{\text{CN}}_4$ ) from slags, and analysis thereof. (Also FRANCK, *J. S. C. I.*, 1897, 942.)

## ALUMINIUM.

A large number of papers dealing with the estimation of aluminium in phosphatic materials, in which the iron is separated with  $\text{NaHO}$ , or the Al estimated by difference after determining the Fe volumetrically, are mostly unnoticed, because such processes are in principle very well known, and in steel works' practice have only a limited application.

The classification is :

- I. SEPARATION FROM OTHER ELEMENTS.
- II. GRAVIMETRIC ESTIMATIONS.
- III. VOLUMETRIC ESTIMATIONS.

### I. Separation from other Elements.

*Iron.* (See also 1775.)

1512. REYNOLDS (*C. N.*, ii., 208).—Add oxalic acid to keep up  $\text{Al}_2\text{O}_3$ , pour into  $\text{AmHO} + \text{Am}_2\text{S}$ , oxidize the filtrate, and precipitate the Al with  $\text{Am}_2\text{CO}_3$ . PISANI (*C. N.*, iii., 257).—Oxalate keeps up the  $\text{Al}_2\text{O}_3$  only for a time; heat readily causes it to separate.
1513. DYER (*C. N.*, liii., 51).—The ammoniacal citrate solution of the oxides is treated with  $\text{Am}_2\text{S}$ , and the ferrous sulphide filtered off.
1514. CARNOT (*C. N.*, xlv., 85).—Add tartaric acid, and precipitate Fe with  $\text{Am}_2\text{S}$ ; Al is precipitated from the acetic filtrate as  $\text{AlPO}_4$ . In order to separate Al from Cr, the latter must be oxidized to  $\text{CrO}_3$ .
1515. WOLFF (*J. C. S.*, lxxx., ii., 198).—From a solution of hydroxides in ammonium salicylate  $\text{H}_2\text{S}$  precipitates Fe completely leaving Al in solution.

1516. DEVILLE (*C. N.*, v., 102).—Heat  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  in  $\text{H} + \text{HCl}$ , and weigh the residual alumina. A similar process is used by L'HÔTÉ (*C. N.*, lv., 176), KONINCK (*C. N.*, lxix., 13), and ROZYCKI (*J. I. S. I.*, 1893, ii., 414).
1517. GOOCH and HAVENS (*C. N.*, lxxx., 39).—Fe is volatilized and separated from Al in  $\text{HCl}$  containing Cl at lower temperatures than with  $\text{HCl}$  alone.
1518. WÖHLER (*C. N.*, xviii., 154).—Boil neutralized solution with thio-sulphate to expulsion of  $\text{SO}_2$ .  $\text{Al}_2\text{O}_3$  is precipitated.
1519. PARNELL (*C. N.*, xxi., 54).—To slightly acid solution add “hypo.” more than equivalent to free acid, and boil only ten or fifteen minutes.
1520. FLIGHT (*C. N.*, xxxi., 214).—Boil faintly acid solution (containing  $\text{P}_2\text{O}_5$ ) for several hours with excess of hypo.
1521. DONATH and JELLER (*J. S. C. I.*, 1887, 458).—After boiling with hypo., the filtrate should be boiled down one-half to recover small amounts of  $\text{Al}_2\text{O}_3$ . The precipitate must be strongly ignited in order to get rid of the sulphur.
1522. ESILMANN (*C. N.*, xxviii., 209).—To warm dilute solution, containing free acid and excess  $\text{P}_2\text{O}_5$ , add hypo. and acetic acid; boil twenty minutes, and collect  $\text{AlPO}_4$ .
1523. WARINGTON (*C. N.*, x., 1).—Precipitate the acid solution (of mineral phosphate) with  $\text{NaHO}$ ; digest, and estimate Al in filtrate. Also JONES (*C. N.*, liii., 87), GLADDING (*C. N.*, lxxiv., 146), and many others.
1524. LASNE (*C. N.*, lxxiv., 309).—As 1523.  $\text{AlPO}_4$  is soluble in acetic solutions. True  $\text{AlPO}_4$  is formed by boiling with hypo. only when a certain excess of  $\text{P}_2\text{O}_5$  is present.
1525. GLASER (*J. C. S.*, lxiv., ii., 346).—The mixed phosphates are fused with  $\text{Na}_2\text{CO}_3$ ; Al can then be completely boiled out with water.
1526. LYTE (*C. N.*, xxviii., 324) and BECKMAN (*C. N.*, xlv., 226).—A boiling solution of  $\text{Ba}(\text{HO})_2$  separates Fe and Al perfectly, and so dispenses with the preparation of pure soda, etc.
1527. GLASER (*J. S. C. I.*, 1897, 936).—To nearly neutral and cold solution add  $\text{Na}_2\text{O}_2$  until the solution becomes quite clear. Boil to decompose sodium ferrate, and filter off  $\text{Fe}_2(\text{HO})_6$ .
1528. THOMSON (*C. N.*, liv., 252).—Add  $\text{AmA}$  to neutral  $\text{FeO}$  solution containing  $\text{P}_2\text{O}_5$ . Separate a little Fe from precipitate with  $\text{NaHO}$ , and estimate as  $\text{AlPO}_4$ . If Mn is present, the first separation is made, omitting  $\text{P}_2\text{O}_5$ . Neither the “ $\text{NaHO}$ ” nor hypo. separation of Al from large amounts of iron is satisfactory.
1529. PARRY and MORGAN (*C. N.*, lxvii., 308).—Mainly as 1528; omitting the  $\text{P}_2\text{O}_5$ , and precipitating finally as  $\text{Al}_2\text{O}_3$ .
1530. DONATH (*C. N.*, xlvi., 12).—Reduce with hypo., pour into alkaline  $\text{KCN}$ , acidify with  $\text{HCl}$ , and precipitate Al with  $\text{Am}_2\text{CO}_3$ . REGELSBERGER (*J. S. C. I.*, 1891, 1033) precipitates the Al finally by boiling with  $\text{AmNO}_3$ .

1531. MOORE (*C. N.*, lvii., 125).—Add excess  $\text{NaHCO}_2$  to  $\text{FeO}$  solution, and then form ferro-cyanide by adding to  $\text{KCN}$ . Boil with  $\text{AmCl}$  to precipitate  $\text{Al}$ . Separates also  $\text{Ni}$  and  $\text{Co}$  from  $\text{Al}$ .
1532. BORNTÄGER (*C. N.*, lxvii., 204).—Precipitate oxides together from neutral solution with potassium oleate, and dissolve out the iron oleate with hot petroleum.
1533. VIGNON (*C. N.*, li., 165).—Mix the solution with large excess of trimethylamine, and allow to stand twenty-four hours; the precipitated  $\text{Al}$  is completely re-dissolved.
1534. HESS and CAMPBELL (*C. N.*, lxxxi., 158).—From neutral and reduced solution precipitate  $\text{Al}$  (together with all the  $\text{P}_2\text{O}_5$ ) with phenylhydrazine.  $\text{Cr}$  is also precipitated; but neither  $\text{Fe}$ ,  $\text{Ca}$ ,  $\text{Mg}$ ,  $\text{Mn}$ ,  $\text{Co}$ , or  $\text{Ni}$  are.
1535. DE KONINCK (*C. N.*, lxii., 19) and BREUTEL (*J. S. C. I.*, 1887, 151).—Add nitroso- $\beta$ -naphthol to acetic acid solution; the  $\text{Fe}$  only is precipitated. (See 323 and 324 for other separations with this reagent.)
1536. GOOCH and HAVENS (*C. N.*, lxxiv., 296).— $\text{Al}_2\text{Cl}_6$  is almost insoluble in etherized  $\text{HCl}$ ;  $\text{Fe}_2\text{Cl}_6$  easily soluble. Precipitated  $\text{Al}_2\text{Cl}_6$  ignited under  $\text{HgO}$  to  $\text{Al}_2\text{O}_3$ .
1537. BEILSTEIN and LUTHER (*C. N.*, lxvi., 37).—Evaporate  $\text{HNO}_3$  solution on water-bath, and dissolve out basic aluminium nitrate with water.
1538. MARCHAL and WIERNIK (*J. C. S.*, lxiv., ii., 49).—Neutralize acid solution and boil with freshly precipitated  $\text{MnO}_2$ . The filtrate contains  $\text{Al}$  (and  $\text{Cr}$ ); the  $\text{Fe}$  remains with the undissolved  $\text{MnO}_2$ .
1539. KOHN and WOODGATE (*J. C. S. I.*, 1889, 260).—Electrolytic separation from oxalate solutions. ENGELS (*J. S. C. I.*, 1898, 796).—From solution containing Rochelle salt.

#### *Manganese:*

1540. GIBBS (*C. N.*, xi., 102).—By boiling neutral solutions with sodium acetate,  $\text{Al}$  is precipitated free from  $\text{Mn}$ ,  $\text{Ni}$ ,  $\text{Co}$ ,  $\text{Zn}$ ,  $\text{Mg}$ ,  $\text{Ca}$ , and  $\text{Ur}$ . A second precipitation is more necessary than in the like  $\text{Fe}$  separation.
1541. LEFFLER (*C. N.*, lxxvii., 265).— $\text{Al}_2\text{Cl}_6 \cdot 11.5\text{Al}_2(\text{HO})_6$  may be formed by neutralizing  $\text{Al}_2\text{Cl}_6$  solutions with dilute alkalis. The acetate precipitation separates  $\text{Mn}$ , but not  $\text{Ni}$ , quantitatively. The separation of  $\text{Ni}$  by  $\text{Na}_3\text{PO}_4$  in acetic solutions is approximately accurate.
1542. *Chromium*.—BREARLEY (*C. N.*, lxxvii., 179).— $\text{Al}$  is not separated from  $\text{CrO}_3$  by precipitating with  $\text{AmHO}$ ,  $\text{Am}_2\text{CO}_3$ , or acetates, and a considerable excess of  $\text{Na}_2\text{CO}_3$  is needed. It may be separated by  $\text{Na}_3\text{PO}_4$  in acetic solutions.

#### *Magnesia and Lime:*

1543. WRINKLE (*C. N.*, xxii., 4).—The amount of  $\text{MgO}$  which goes down on precipitating  $\text{Al}$  with  $\text{AmHO}$  depends on the presence of  $\text{SO}_3$  and the mode of adding  $\text{AmHO}$ .

1544. ROSE (*C. N.*, ii., 291).—By adding AmHO and boiling off excess, any Ca precipitated by CO<sub>2</sub> impurities is re-dissolved if ammonium salts are present.

*Copper, Zinc, Mercury, etc.:*

1545. HAVENS (*C. N.*, lxxviii., 53).—Cu, Zn, Hg, and Bi are separated as in 1536.
1546. JANNASCH (*J. S. C.*, lxxvi., ii., 60.)—Hg is precipitated by ammoniacal hydroxylamine in the presence of oxalic acid.
1547. Zircon.—DAVIS (*C. N.*, lix., 100).—Zr is precipitated from nearly neutral solutions with sodium iodate. Al remains in solution. (See 1573.)

*Beryllium:*

1548. ZIMMERMANN (*C. N.*, lviii., 49).—Boil with KHO; Be is precipitated. Or boil neutral solution with hypo.; Al is precipitated.
1549. HAVENS (*C. N.*, lxxvi., 111).—As in 1536.

## II. Gravimetric Estimations.

1550. PENFIELD and HARPER (*C. N.*, liv., 91).—Some instructive experiments on the precipitation and washing of Al<sub>2</sub>(HO)<sub>6</sub>.
1551. GUYARD (*C. N.*, xlviii., 119).—Alumina precipitated in the presence of glycerin falls in dense flocks which are easily washed.
1552. LUCKOW (*C. N.*, xi., 205).—Precipitate with bicarbonates rather than carbonates, as the precipitate is less bulky and more easily washed. The smaller excess of AmHO and larger of Am<sub>2</sub>S used for precipitating the better. Cochineal colours Al solutions carmine.
1553. ALLEN and GOTTSCHALK (*J. S. C. I.*, 1900, 1149).—The Al is precipitated as basic carbonate by passing CO<sub>2</sub> into a solution which contains only a small excess of KHO.
1554. MOISSAN (*C. N.*, lxxiii., 49).—Am<sub>2</sub>S (with reasons), and not AmHO, is used for precipitating Al. Al<sub>2</sub>O<sub>3</sub> is difficult to dehydrate. Estimates also Si, Fe, Cu, and Na in Al alloys.
1555. LUNGE (*J. S. C. I.*, 1890, 111).—On precipitating Al with AmHO, the excess need not be boiled off if AmCl is present; the precipitate retains no SO<sub>3</sub>.
1556. STEAD (*J. S. C. I.*, 1889, 966).—Dissolve Fe in HCl, separate SiO<sub>2</sub>, and boil nearly neutral solution with Na<sub>3</sub>PO<sub>4</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Dissolve precipitated AlPO<sub>4</sub> in HCl, separate little Fe with NaHO and re-precipitate Al as before. PHILLIPS (*C. N.*, lxi., 313) describes a similar process, and so does CARNOT (*C. N.*, lxiii., 10 and 172), except that the AlPO<sub>4</sub> first obtained is purified by re-precipitating with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.
1557. OSMOND (*J. I. S. I.*, 1890, ii., 200).—Heat steel in current of HCl; the Al in the residue is estimated by difference after deducting S and P.



1558. DROWN and M'KENNA (*C. N.*, lxiv., 194).—The steel solution, freed from C and  $\text{SiO}_2$ , is electrolyzed, using Hg cathode. The Fe forms an amalgam, and the Al is precipitated from filtered solution as  $\text{AlPO}_4$ .
1559. SPATZ (*J. C. S.*, lxxx., ii., 349).—Electrolyze oxalate solution of steel; no Al is precipitated until all the Fe is deposited.  $\text{AlPO}_4$  and a little  $\text{FePO}_4$  are precipitated together, and the latter estimated volumetrically and allowed for.
1560. SCHÆNISS (*J. I. S. I.*, 1892, ii., 518).—Evaporate  $\text{HNO}_3$  solution, fuse evaporated residue with NaHO in silver dish, and precipitate Al from acidulated filtrate with AmHO.
1561. ZEIGLER (*C. N.*, lxvi., 321).—Fuse powder (with or without oxidation by acids), and precipitate as  $\text{Al}_2(\text{HO})_6$  after filtering off the iron.
1562. ZIEGLER (*J. I. S. I.*, 1891, i., 440).—Dissolve Fe in HCl, complete reduction to FeO with hypophosphite, and add excess ZnO. Dissolve precipitate in HCl, and eliminate impurities by precipitating with AmHO both before and after fusing with sodium carbonate.
1563. LEDEBUR (*J. I. S. I.*, 1893, ii., 534).—Treat strong HCl solution of  $\text{Fe}_2\text{Cl}_6$  with ether (see 1536). Precipitate Al in aqueous solution as  $\text{AlPO}_4$  with  $\text{Na}_3\text{PO}_4$  and acetate.
1564. KLEMP (*C. N.*, lxii., 241).—Treat Al metal with KHO, burn liberated H to  $\text{H}_2\text{O}$  and calculate per cent. Al from increased weight of  $\text{H}_2\text{SO}_4$  tube.
1565. REGELSBERGER (*J. C. S.*, lxii., 102 and 535).—Dissolve Al metal in KHO, boil with Am $\text{NO}_3$ , and collect precipitated  $\text{Al}_2\text{O}_3$ . KHO completely dissolves Al from its Ni or Cu alloy.
1566. REGELSBERGER (*J. C. S.*, lxiv., ii., 48).—Estimate Al in Fe-Al alloy by process 1530; gives means of analyzing Al-Cu and Al-Zn alloys. JUPTNER (*J. C. S.*, lxiv., ii., 391) calls 1530 Neuhausen's method.
1567. THOMSON (*J. S. C. I.*, 1886, 152).—Precipitate Al and Fe together as phosphates, and determine Fe volumetrically and Al by difference.  $\text{AlPO}_4$  becomes basic on washing with  $\text{H}_2\text{O}$ .
1568. MACIVOR (*C. N.*, xxix., 199).—The ignited  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  are dissolved in  $\text{H}_2\text{SO}_4$  in the presence of zinc prior to the Fe titration.
1569. GLASER (*J. C. S.*, lxii., 1523).—Precipitation of Al solution containing excess  $\text{P}_2\text{O}_5$  with AmHO or Am $\bar{\text{A}}$  at  $100^\circ$  gives basic phosphates; at  $70^\circ$   $\text{AlPO}_4$  exactly is formed.
1570. HUNT, CLAPP, and HANDY (*C. N.*, lxv., 223 and 235).—Analysis of Al metal. Al estimated as  $\text{AlPO}_4$  by boiling with hypo.
1571. HANDY (*C. N.*, lxxv., 55, 66, 79).—Estimation of Cu, Fe, Si (total and graphitic), Na and C in Al.  $\text{Al}_2\text{O}_3$  is very hygroscopic. Analysis of the Cu, Ni, Mn, Cr, W, Ti, and Zn alloys of Al, Al solders, and the raw materials of Al manufacture.
1572. CAMP (*C. N.*, lxxxii., 9).—In ore and cinders the HCl filtrate from  $\text{SiO}_2$  is neutralized and  $\text{AlPO}_4$  precipitated by boiling with Am $\bar{\text{A}}$  and hypo.  $\text{AlPO}_4$  is slightly soluble in the wash-water.

1573. STOCK (*J. S. C. I.*, 1900, 276).—On adding KI and KIO<sub>3</sub> to Al solutions, the precipitated Al<sub>2</sub>(HO)<sub>6</sub> is more easily washed than when formed with AmHO. (See 1547.)

### III. Volumetric Estimations.

1574. REISS (*C. N.*, xlvii., 248).—To boiling acetic solution containing CaCl<sub>2</sub> add standard Am $\bar{O}$  until a turbidity appears;  $3 \text{ Am}\bar{O} = 1 \text{ Al}_2\text{O}_3$ .
1575. PRUNIER (*C. N.*, l., 235).—The neutral solution of Al, using tropæoline indicator, is precipitated by N/2AmHO, and the excess determined in a fraction of the filtrate.
1576. NEUMANN (*J. C. S.*, lxxviii., ii., 64).—Precipitate with standard alkaline sulphide, add H<sub>2</sub>SO<sub>4</sub> to portion of filtrate, and titrate with KHO.
1577. LESCŒUR (*J. C. S.*, lxxiv., ii., 484).—Make solution neutral to helianthin, add excess of alkali, boil, and titrate back with acid, using phenolphthalein.
1578. BAYER (*C. N.*, lii., 277).—Add NaHO in excess, and titrate with litmus as indicator in one portion and tropæoline in another. ATKINSON (*C. N.*, lii., 311) uses phenolphthalein instead of litmus. See also BAYER (*C. N.*, liii., 40), LUNGE (*J. S. C. I.*, 1890, 767), CROSS and BEVAN (*J. S. C. I.*, 1890, 202; and 1891, 314), E. B. (*J. C. S.*, l., 651), and GYZANDER (*C. N.*, lxxxiv., 296).
1579. KRETZSCHMAR (*J. S. C. I.*, 1890, 1064).—Add standard Na<sub>3</sub>PO<sub>4</sub> and Am $\bar{A}$ , and determine excess of P<sub>2</sub>O<sub>5</sub> with uranium acetate. Any Fe present is estimated with KMnO<sub>4</sub>, and its FePO<sub>4</sub> equivalent deducted.

## COPPER.

The items are arranged under the following heads :

- I. SEPARATIONS FROM OTHER METALS.
- II. GRAVIMETRIC ESTIMATIONS.
- III. VOLUMETRIC ESTIMATIONS.
  - a. Cyanide Process.
  - b. Iodide Process.
  - c. Other Processes.
- IV. COLORIMETRIC ESTIMATION.
- V. DETECTION.
- VI. MISCELLANEOUS NOTES.

## I. Separations from other Metals.

*Iron.* (See also 1095, 1603, 1646, 1650, 1719.)

- 1580. LOEWE (*C. N.*, i., 119).—After precipitating with  $\text{AmHO}$ , the  $\text{Fe}_2(\text{HO})_6$  cannot be *washed* free from Cu ; it must be dissolved and re-precipitated.
- 1581. GALETTI (*C. N.*, xx., 248).—Precipitate iron with  $\text{AmHO}$ , add excess acetic acid, and again excess  $\text{AmHO}$  followed by acetic. This procedure prevents adhesion of Cu to precipitated iron. Cu titrated with ferro-cyanide.
- 1582. MERRICK (*C. N.*, xxvi., 115).—Decompose pyrites with  $\text{HNO}_3$ , evaporate, and dissolve Cu from residue with dilute  $\text{AmHO}$ . (See also 1629 and 1647.)
- 1583. BREARLEY (*C. N.*, lxxviii., 14).—Iron can be precipitated from neutralized solutions as basic chromate perfectly free from copper, and Cu estimated as in 1679.
- 1584. FLAJOLOT (*C. N.*, ix., 193).—Precipitate Cu with hypo. The precipitate is free from Fe, Zn, Co, Ni, and P, but not As or Sb. Estimate Cu with KCN.
- 1585. CARNOT (*C. N.*, liii., 172).—As 1584. Precipitated  $\text{Cu}_2\text{S}$  ignited with S in H and weighed.
- 1586. VORTMANN (*J. C. S.*, lxvi., ii., 35).— $\text{AmHO}$  solutions of Cu electrolyzed without filtering off precipitated Fe.
- 1587. FERNBERGER and SMITH (*J. S. C. I.*, 1900, 53).—Electro-separations of Fe, Cr, Zn, Ni, Co, Mn, etc., from Cu, using solutions of the phosphates in phosphoric acid.
- 1588. *Aluminium.*—HUNT, CLAPP, and HANDY (*C. N.*, lxxv., 225).—Cu precipitated with  $\text{H}_2\text{S}$  from acid solution of metallic Al, evaporated with  $\text{HNO}_3$ , and weighed as  $\text{CuO}$ .

*Zinc.* (See also 1584, 1587, 1627, 1633, 1650, 1652.)

1589. WITTSTEIN (*C. N.*, xix., 156).—Zn dissolved from precipitated sulphides with dilute  $\text{H}_2\text{SO}_4$ .
1590. BERGLUND (*C. N.*, xlvii., 244).—Precipitate Cu with  $\text{H}_2\text{S}$  from definitely acidified solutions.
1591. KNORRE (*C. N.*, lix., 222).—Precipitate Cu with nitroso- $\beta$ -naphthol, and ignite to CuO. (See 323 and 324.)
1592. KAIKOW (*J. C. S.*, lxviii., ii., 246).—Cu precipitated with hydrazine hydrochloride and KI. (See 1151 and 1652.)
1593. SODERBAUM (*J. C. S.*, lxxii., ii., 348).—Cu is precipitated by a stream of acetylene quite free from zinc.
1594. MAWROW and MUTHMANN (*J. S. C. I.*, 1896, 381).—Cu is precipitated free from Zn and Cd, if no HCl is present, by adding hypophosphorous acid.

*Cadmium.* (See also 324, 1594, 1603, 1633, 1641, 1651.)

1595. BEHAL (*C. N.*, li., 280) and WARREN (*C. N.*, lxix., 125).—Add an alkaline solution of sodium tartrate and boil. Cd is precipitated.
1596. GUCCI (*C. N.*, li., 55).—Precipitate Cu with ammonium benzoate from acid solution.
1597. VORTMANN (*C. N.*, xlv., 57).—Hypo. precipitates Cu free from Cd.
1598. HOFFMANN (*C. N.*, ii., 159).—Cd is easily dissolved from mixed sulphides with  $\text{H}_2\text{SO}_4$ .
1599. BROWNING (*J. C. S.*, lxvi., ii., 68).—Cu precipitated as iodide, dried, and weighed; Cd in solution.
1600. BACKELANDT (*J. S. C. I.*, 1886, 510).—Cd is precipitated with KHO in the presence of glycerol. Cu is precipitated from the filtrate with glucose and weighed as CuO.
1601. WELLS (*C. N.*, lxiv., 294).—To neutral solution add hypo. until all colour goes; then precipitate Cd with  $\text{Na}_2\text{CO}_3$  and filter off. On acidifying filtrate, Cu is precipitated.
1602. BORNEMANN (*C. N.*, lxxxi., 53).—Cu precipitated from hot  $\text{HNO}_3$  solutions with oxalic acid.

*Nickel.* (See also 1587, 1646, 1650.)

1603. RUDORFF (Ag, Hg, Cd) (*J. C. S.*, lxiv., ii., 305) and SMITH and MOYER (Cd, Zn, Co, Fe) (*J. C. S.*, lxiv., ii., 496).—Electro-separations.

*Mercury.* (See also 1694.)

1604. ROSENBLADT (*J. C. S.*, lii., 302).—Precipitated sulphides digested with K thiocarbonate. Hg and Pd dissolved.
1605. VON USLAR (*C. N.*, lxxiii., 28).—Precipitate Hg as  $\text{Hg}_2\text{Cl}_2$  with phosphorous acid from acidified solutions.
1606. JANNASCH (*C. N.*, lxxiv., 145).—Hg volatilized from precipitated sulphides; or (*J. C. S.*, lxxvi., ii., 59), precipitated from  $\text{AmHO}$  solutions with hydroxylamine.

1607. SMITH and MACAULEY (*J. C. S.*, lvi., 797 ; and lxii., 239) and REVAY (Hg and As) (*C. N.*, lxxix., 194).—Electro-separations.

*Lead.* (See also 1634, 1694.)

1608. NISSENSON (*J. C. S.*, lxvi., ii., 220) and CLASSEN (*J. C. S.*, liv., 529).—Electro-separations.

*Arsenic.* (See also 1641, 1651, 1652, 1665, 1705.)

1609. PARNELL (*C. N.*, xxi., 133).—Examines processes depending on solubility of As in  $\text{Na}_2\text{S}$ , passing chlorine through alkaline liquor containing precipitated sulphides, and heating in Cl gas and H.
1610. CLASSEN (*J. C. S.*, liv., 528).—By volatilizing As from HCl solution.
1611. JANNASCH (Sb and Sn) (*J. C. S.*, lxviii., ii., 89 and 462).—By volatilizing in a stream of HCl gas.
1612. GUCCI (*J. C. S.*, liv., 630).—Cu precipitated with KHO.
1613. M'KAY (*J. S. C. I.*, 1890, 822), SMITH and FRANKEL (*J. S. C. I.*, 1890, 1067), and SCHMUCKER (*J. S. C. I.*, 1894, 280).—Electrolytic.

*Antimony.* (See also 1611, 1659, 1665.)

1614. LUCAS (*C. N.*, lxxix., 78).—Treat mixed sulphides with  $\text{Na}_2\text{S}$ , destroy polysulphides with  $\text{H}_2\text{O}_2$ , and electro-deposit Sb without removing CuS, as in 1130.
1615. FINKENER (*J. S. C. I.*, 1889, 733). Add alkaline fluoride, and then KI and  $\text{SO}_2$ . The filtrate contains  $\text{Sb}_2\text{O}_3$  and a little Cu, which are separated with  $\text{H}_2\text{S}$  and  $\text{Am}_2\text{S}$ .
1616. SMITH and WALLACE (*J. S. C. I.*, 1893, 1063).—Electro-separation.

*Bismuth :*

1617. LOWE (*C. N.*, xlviii., 296).—Precipitate with NaHO, re-dissolve in glycerin, and precipitate Cu with glucose in the cold. Bi in solution.
1618. JANNASCH (*J. C. S.*, lxvi., ii., 71).—Bi precipitated with AmHO and  $\text{H}_2\text{O}_2$ .
1619. SMITH and SALTAR (*J. S. C. I.*, 1893, 605).—Electro-separation from a citrate solution containing regulated amount of KCN.

*Silver.* (See also 1603, 1694.)

1620. REVAY (*J. S. C. I.*, 1898, 184) and KUSTER and STEINWEHR (*J. S. C. I.*, 1898, 466).—Electro-separations.

*Selenium :*

1621. VIOLETTE (*C. N.*, xxi., 178).—Heat strongly in current of dry air ; the Se is sublimed as a white crystalline ring.

*Palladium.* (See also 1604.)

1622. WÖHLER (*C. N.* xv., 40).—Cu precipitated with  $\text{SO}_2$  and KCNS.

*Thallium :*

1623. CROOKES (*C. N.*, vii., 133 and 218).—Precipitate Tl as sulphide from alkaline cyanide solution ; or, precipitate metals as subiodides and dissolve out the Cu with AmHO. Metallic Cu frequently contains Tl

**II. Gravimetric Estimations.**

1624. STORER (*C. N.*, iii., 70).—Deposit Cu from  $H_2SO_4$  solutions with iron and heat in nitrogen before weighing to destroy organic matter.
1625. KERN (*C. N.*, xxxi., 76).—Cu-Sn-Zn alloys, after decomposition, are precipitated as metals on Fe, Zn, etc.
1626. VILLIERS (*C. N.*, lxxviii., 263).—Precipitate Cu with Mg, wash with alcohol, dry at  $100^\circ C.$ , and weigh. An alloy is precipitated if Zn is present.
1627. WARREN (*C. N.*, lxi., 136 ; and lxxi., 92).—Decompose Zn-Cu alloy with strong  $H_2SO_4$ , precipitate Cu with Mg, and weigh. After adding sodium acetate, Zn may be precipitated similarly.
1628. SHENGLE and SMITH (*C. N.*, lxxxii., 134).—Cu precipitated by zinc always contains more or less of the latter metal.
1629. MOHR (*C. N.*, vi., 229).—Decompose ore with  $H_2SO_4$ , evaporate, and boil dry residue with water. Cu and a little Fe dissolve ; precipitate Cu with Zn and wash out of contact with air.
1630. SUTTON (*C. N.*, vi., 275).—A score of common elements have no influence on 1629.<sup>1</sup>
1631. LOWE (*C. N.*, ii., 191).—Cu is completely precipitated by a slight excess of oxalic acid. (See 1704.)
1632. GIBBS (*C. N.*, xvii., 172).—Cu is completely precipitated by boiling with small excess of  $Na_2CO_3$ . The metal reduced in H is free from alkalis. (See also FIELD, *C. N.*, ii., 279.)
1633. WARREN (*C. N.*, lxiii., 193).—Precipitate with glucose from solution containing NaHO and Rochelle salt and weigh as CuO. Zn and Cd perfectly separated. For various means of estimating the suboxide precipitated by glucose, see *C. N.*, xlv., 262.
1634. JANNASCH and LEZCINSKY (*C. N.*, lxix., 7).—Separate Pb from AmH() solution with  $H_2O_2$ . Precipitate Cu in  $H_2S$  and heat in air which has passed through  $Am_2CO_3$ , so as to decompose any  $CuSO_4$  formed.
1635. MILLON and COMMAILE (*C. N.*, viii., 100).—Copper always escapes with the nitrous vapours on heating  $Cu(NO_3)_2$ . Weigh as Cu after reducing in H.
1636. WEGSCHEIDER (*J. C. S.*, lxvi., ii., 31).—Particulars of temperature and nature of atmosphere to be attained when Cu is estimated as cuprous sulphide. (See also 1688.)

<sup>1</sup> Simple replacement of copper by either Zn, Mg, or Fe is found in no case to be exactly true. Clowes's paper (*C. N.*, lxxviii., 155) may be taken as a type of many others.

1637. DEBRAY and JOANNIS (*C. N.*, l., 234 and 248).—A temperature high enough to melt or even frit CuO partly decomposes it.
1638. ULRICI (*C. N.*, xx., 118).—Ignited precipitate formed with  $H_2S$  is weighed as though  $Cu_2S$ , but really it is always a mixture of CuO and  $Cu_2S$ . (See also 1688.)
1639. HOLTHOF (*C. N.*, lxi., 193).—Precipitated sulphide ignited while moist passes to oxide completely. Dried precipitates contain  $SO_3$  after ignition.
1640. STICKNEY (*J. C. S.*, lxx., ii., 523).— $Cu_2S$  is reduced to copper when heated in contact with a Bunsen flame.
1641. NISSENSON and NEUMANN (*J. C. S.*, lxx., ii., 450).—Cu precipitated with hypo. is oxidized completely to CuO in the muffle. Any As is expelled. Cd does not interfere. Also WILLENZ (*J. C. S.*, lxxviii., ii., 315).
1642. TROILIUS (*J. I. S. I.*, 1883, 367 and 710).—Precipitate  $H_2SO_4$  solution of steel with hypo.; re-dissolve and re-precipitate, and ignite moist precipitate to CuO.
1643. REINHARDT (*J. I. S. I.*, 1889, ii., 481).—Reduce ferric solution with hypophosphite and precipitate Cu with  $H_2S$ .  $H_2SO_4$  (3 : 1) dissolves basic pig without attacking contained copper.
1644. ZIEGLER (*J. S. C. I.*, 1893, 377).—Ammonium sulpho-carbonate, which is more agreeable in use than  $H_2S$ , precipitates Cu from FeO solutions of steel.
1645. REIS (*J. I. S. I.*, 1891, i., 441).—HCl solution of steel is treated with  $H_2O_2$  to bring any undissolved Cu into solution; then reduced as 1643, and Cu precipitated with sulpho-carbonate and ignited to oxide.
1646. KLEIN (*J. S. C. I.*, 1887, 836).—Add ammonium dithiocarbamate to hot HCl solution. Ignite precipitate with S in H and weigh as  $Cu_2S$ . Fe, Mn, and Ni do not interfere.
1647. PARRY and MORGAN (*C. N.*, lxxvii., 259).—Precipitate from FeO solution with  $H_2S$  or hypo., and re-precipitate with NaHO or ignite at once to CuO. Also, digest nearly dried residue of 20 to 50 grms. of steel with AmHO and compare blue colour with standards.
1648. NAHUSEN (*C. N.*, lx., 133).—Decompose pyrites with  $H_2SO_4 + HNO_3$ , precipitate with  $H_2S$ , dissolve out As and Sb with  $Na_2S$ , and estimate Cu as sulphide.
1649. BLOXAM (*C. N.*, xi., 196).—On digesting the sulphide with  $Am_2S$ , a portion of the Cu dissolves as  $Cu_2(NH_4)_2S_7$ .
1650. GIBBS (*C. N.*, xvii., 160).—Precipitate from  $H_2SO_4$  solution with Mg hypophosphite, ignite in H, and weigh as Cu. Fe, Mn, Ni, and Zn do not interfere; Sb, As, HCl, and  $HNO_3$  do.
1651. SODERBAUM (*J. S. C. I.*, 1897, 563).—Cu precipitated from alkaline solution with acetylene. Dissolve acetylide in  $HNO_3$ , filter from C, evaporate, and ignite to CuO. *J. C. S.*, lxxiv., ii., 191.—As and Cd are separated from Cu in this way.

1652. JANNASCH and BIEDERMANN (*C. N.*, lxxxii., 282).—Hydrazine sulphate precipitates metallic Cu from NaHO solutions free from Zn, As, and nearly Sn. Cu weighed as CuO.
1653. TAMM (*C. N.*, xxiv., 91).—Precipitate as sulpho-cyanide (see 1694), digest with  $\text{Am}_2\text{S}$ , and weigh as  $\text{Cu}_2\text{S}$ . Cu may be separated as CuCNS from all other elements.
1654. NAMA (*C. N.*, lxxxiii., 258).—Precipitation as CuCNS with variations in AmCNS,  $\text{H}_2\text{SO}_4$ , drying period, etc. See also COHN (*J. S. C. I.*, 1901, 1243).
1655. MILLON and COMMAILE (*C. N.*, vii., 218).—Process for estimating Cu (or Ag) or mixtures of CuO and  $\text{Cu}_2\text{O}$  is based on the fact that AmHO solutions of  $\text{Cu}_2\text{O}$  precipitate Ag from silver solutions.
1656. GIBBS (*C. N.*, xi., 173).—Precipitation with Zn accurate. (See 1628.) Suggests electro-deposition from sulphate solutions.
1657. LUCKOW (*C. N.*, xix., 221).—Dissolve roasted ore in acid and electro-deposit Cu. Behaviour of associated elements.
1658. HAMPE (*C. N.*, lxvii., 103).—Small quantities of Sb are always electro-deposited with Cu. So also is Bi (*C. N.*, lxviii., 51). The Bi may be removed as oxychloride (STAHL, *J. C. S.*, lii., 529). See also SMITH and SALTAR (*J. C. S.*, lxiv., ii., 495), who say Pb is also deposited.
1659. SMITH and WALLACE (*J. C. S.*, lxiv., ii., 495).—No Sb is deposited with the Cu from AmHO tartaric solutions.
1660. CHASSY (*C. N.*, lxx., 97).—On electrolysis a heated  $\text{CuSO}_4$  solution deposits  $\text{Cu}_2\text{O}$ .
1661. MERRICK (*C. N.*, xxxiii., 111).—Can determine 0.0001 gram. Cu by depositing on Pt.
1662. MACKINTOSH (*C. N.*, xlv., 279; and xlv., 101).—Deposition from nitro-citric acid solutions too high; from  $\text{HNO}_3$  alone difficult to precipitate all the Cu.  $\text{CuSO}_4$  solutions best.
1663. RUDORFF (*J. C. S.*, lxiv., ii., 93).—From faintly  $\text{HNO}_3$ —or, if Cl is present, from AmHO—solutions. Sodium acetate is added before stopping the current.
1664. DROSSBACH (*J. C. S.*, lxiv., ii., 93).—Electrolyze AmHO solutions only until the Cu is precipitated. Hg, Cd, Pb, and Ag are the only interfering elements.
1665. CETTEL (*J. C. S.*, lxviii., ii., 139).—Best deposited from AmHO solution if Cl, As, or Sb are present. Pb, Bi, Hg, Cd, and Ni interfere.
1666. CLASSEN (*J. C. S.*, xlviii., 1095; and lvi., 77) and WAGNER (*J. C. S.*, lxxii., ii., 520).—Deposit from oxalate solutions at 70—80° C.
1667. HOLLARD (*C. N.*, lxxvi., 31).—Electrolytic methods for complete analysis of brass and bronze.
1668. BRAND (*J. S. C. I.*, 1889, 1011).—From pyrophosphate solutions.
1669. WOLMAN (*J. C. S.*, lxxiv., ii., 50).—Best results obtained by deposition from  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  solutions. Also SMITH (*J. S. C. I.*, 1901, 750).
1670. MOORE (*C. N.*, liii., 209).—Deposits from alkaline KCN solutions at 70°.



## III. Volumetric Estimations.

*a. Cyanide Process.* (See also 1690.)

1671. FIELD (*C. N.*, i., 25, etc.).—Not necessary to filter off precipitated  $\text{Fe}_2(\text{HO})_6$ . Arsenic easily separated from KCN solution. Hg, Ag, Zn, Ni, Co, and Mn interfere. Describes also the following methods:—Titration with alkaline sulphide (Pelouze); reduction to  $\text{Cu}_2\text{O}$  and titration with permanganate (Treille); precipitation with sugar and titration with permanganate (Mohr); titration with  $\text{Fe}_2\text{Cl}_6$  and  $\text{KMnO}_4$  (Schwarz); precipitation of Cu with Fe and estimation in various ways; titration with KI and  $\text{K}_2\text{Cr}_2\text{O}_7$  (Streng); estimating metal used in reducing CuO to  $\text{Cu}_2\text{O}$ ; the iodide process; colour comparison of AmHO solutions; weighing as  $\text{Cu}_2\text{S} + \text{CuO}$ ; and the sulpho-cyanide process (Rivot).
1672. FLECK (*C. N.*, ii., 35).—Results vary with excess of AmHO; uses  $\text{Am}_2\text{CO}_3$  instead; and an indicator for end-reaction.
1673. STEINBECK (*C. N.*, xix., 207).—Precipitate Cu from solution of ore with Zn and Pt, dissolve in  $\text{HNO}_3$ , and titrate. Influence of Pb, Zn, AmHO compounds and heat observed.
1674. THOMSON (*C. N.*, xxxiii., 152).—Observes influence of many elements on titration; that of Zn, Cd, Mn, Ni, Sn, Hg, Ag, Au, Pt, and Pd most pronounced. AmHO and its salts cause variations.
1675. ULBRICHT (*C. N.*, xlv., 82).—Sample to be treated exactly as standard, and to be as nearly as possible identical.
1676. BERINGER (*C. N.*, xlviii., 111).—Results influenced by mode of operation and temperature. AmHO exerts same influence whether as sulphate, nitrate, or chloride. Sodium salts without influence, except carbonate, sulphite, and nitrite. Determines conditions under which proportional results are obtained.
1677. DAVIES (*C. N.*, lviii., 131).—Results are more concordant when the solution is made alkaline with  $\text{Na}_2\text{CO}_3$  instead of AmHO.
1678. FESSENDEN (*C. N.*, lxi., 183 and 253).—Confirms 1677; the end-reaction is more decided.
1679. BREARLEY (*C. N.*, lxxvi., 189).—The AgI indicator (1188) is applied to the KCN estimation. The results are better, particularly when the solution is made alkaline with  $\text{Na}_2\text{CO}_3$ .
1680. BREARLEY (*C. N.*, lxxvi., 291, 303).—Influence of many elements on 1679 process observed. Interference of Zn, Mn, and Cd avoided;  $\text{Cr}_2\text{O}_3$  salts injurious. Organic acids and pyrophosphate used to keep precipitable bodies in solution.
1681. DONATH and TELLER (*C. N.*, lvii., 102).—Ore ignited with Zn powder, boiled with  $\text{H}_2\text{SO}_4$ , Cu dissolved from associated gangue with  $\text{HNO}_3$ , and titrated with KCN.
1682. JOHNSON (*J. S. C. I.*, 1889, 603).—Cu precipitated from solution of pyrites with KCNS and  $\text{SnCl}_2$ , dissolved in nitro-hydrochloric, and

- titrated with KCN ; or the CuCNS dissolved in  $\text{Fe}_2(\text{SO}_4)_3$  and resulting FeO titrated with  $\text{KMnO}_4$ .  $\text{SnCl}_2$  is better than any other reducer.
1683. ELLIS (*J. S. C. I.*, 1889, 686).—Tabulated results showing influence of zinc. The solution may stand an indefinite time after adding  $\text{AmHO}$  without spoiling.
1684. CLENNELL (*J. S. C. I.*, 1900, 14).—Cu in KCN solutions estimated by adding  $\text{H}_2\text{SO}_4$  until a precipitate of  $\text{Cu}(\text{CN})_2$  appears, then an excess of  $\text{H}_2\text{SO}_4$ , and finally titrating the free acid in a fraction of the filtrate with  $\text{Na}_2\text{CO}_3$ .

*b. Iodide Process.* (See also 1701.)

1685. WESTMORELAND (*J. S. C. I.*, 1886, 48).—Analysis of ores, pyrites, etc. Neither Ag, Zn, Cd, As, Bi, Mn, or Sn interfere ; nor does Fe materially in the presence of  $\text{Na}_3\text{PO}_4$  or  $\text{As}_2\text{O}_3$ . Also critical account of the electrolytic and dry assay processes and the assay of Au in bar Cu.
1686. WESTMORELAND (*C. N.*, lviii., 76, 108, and 132).—Shows that the iodide process is superior to the electrolytic for all kinds of Cu compounds.
1687. WILLIAMS (*C. N.*, lviii., 272).—Pb and As exert a prejudicial effect on the titration.
1688. HAUPT (*C. N.*, lxx., 206).—Titration not interfered with by Zn or Pb ; it is by Ni and Fe. Cu precipitated from Fe solutions with Zn. KI detects one Cu in 500,000. Experiments on the ignition of  $\text{Cu}_2\text{S}$ .
1689. BRUYN and VAN LEENT (*J. C. S.*, lxii., 753).—Operate in stoppered flasks. Ni, Mn, and Fe as sulphates and free acid do not interfere ; Bi does.
1690. DULIN (*C. N.*, lxxii., 70).—Describes KCN method and its limitations, KI process influenced by large amounts of alkaline salts and Bi. For either titration first precipitate Cu with Al. Electro-deposition from solutions containing much  $\text{HNO}_3$ .
1691. LOW (*C. N.*, lxxiv., 52).—First precipitate Cu with Al ; then neither Ag, Pb, Bi, or As interfere. Procedure for ores.
1692. WILLENZ (*C. N.*, lxxvi., 243).—KI process applied to estimation of Cu in pyrites.
1693. SHELBY (*J. S. C. I.*, 1900, 776).—FeO formed by hypo. and then sheet Zn added. Nascent H and the previously liberated S form  $\text{H}_2\text{S}$ , which precipitates the Cu. Estimation with KI or KCN after dissolving in  $\text{HNO}_3$ , etc.

*c. Various Volumetric Processes.* (See also 1682.)

1694. FLEISCHER (*C. N.*, xix., 206).—Precipitate as subiodide with KI and  $\text{SnCl}_2$ , dissolve precipitate in  $\text{Fe}_2(\text{SO}_4)_3$ , and titrate FeO with  $\text{KMnO}_4$ . Or, precipitate Cu with KCNS and  $\text{SO}_2$ , digest CuCNS with  $\text{NaHO}$ , and estimate  $\text{Cu}_2\text{O}$  as before. Pb, Ag, and Hg are the only interfering metals, and these are separated with  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , and  $\text{SnCl}_2$  respectively.

1695. HENRIQUES (*J. C. S.*, lxiv., ii., 345). — Precipitate with  $\text{SO}_2$  and standard KCNS. Estimate excess KCNS with  $\text{AgNO}_3$  and  $\text{Fe}_2(\text{SO}_4)_3$  indicator.
1696. MEADE (*C. N.*, lxxx., 67).—Decompose precipitated CuCNS with KHO, add collected  $\text{Cu}_2(\text{OH})_2$  to acid  $\text{Fe}_2(\text{SO}_4)_3$ , and titrate FeO with  $\text{KMnO}_4$ .
1697. PARR (*J. S. C. I.*, 1900, 1148).—Decompose CuCNS with NaHO destroy  $\text{Cu}_2(\text{OH})_2$  with  $\text{KMnO}_4$  in alkaline liquid, then acidify and titrate KCNS with  $\text{KMnO}_4$ . 1 c.c. N/10 $\text{KMnO}_4$  = 0.0009 Cu.
1698. CAVEN and HILL (*J. S. C. I.*, 1897, 981).—Add  $\text{Cu}_2\text{O}$  to excess  $\text{KMnO}_4$  in  $\text{H}_2\text{SO}_4$  and titrate un-reduced portion with oxalic acid.
1699. DEDERICHS (*J. C. S.*, lxxvi., ii., 813).—Digest  $\text{HNO}_3$  solution of brass with  $\text{NaHSO}_3$ , add standard AmCNS, and titrate excess with  $\text{AgNO}_3$  in aliquot filtrate.
1700. ZECCHINI (*J. S. C. I.*, 1899, 710).—Add excess of solution containing hypo. and AmCNS and titrate with iodine. Neither AmCNS nor CuCNS react with iodine.
1701. GARRIGUES (*C. N.*, lxxvii., 41 and 52).—End-point of iodide process sharper in  $\text{H}_2\text{SO}_4$  than in  $\text{C}_2\text{H}_4\text{O}_2$  solution. Decompose precipitated CuCNS with standard NaHO and titrate excess with acid and methyl-orange. Conjoint presence of Zn and Sb interfere. Some important points in the analysis of bearing-metals, bronzes, etc.
1702. WEIL (*C. N.*, xxiii., 49 ; and xlv., 284).—HCl solution of Cu titrated at boiling-point with  $\text{SnCl}_2$  to decolorization.  $\text{HgCl}_2$  may be used as indicator. Fe and Ni interfere.
1703. JEAN (*J. C. S.*, lxiv., ii., 493).—Estimation of Cu, Fe, Sb, and Zn in minerals by Weil's process.
1704. PETERS (*C. N.*, lxxxiii., 221, etc.).—Moderate amounts of Cu are precipitated as oxalate in  $\text{HNO}_3$  solutions and titrated with  $\text{KMnO}_4$ . Cd, As, Sn, and Fe are separated.
1705. KUNSEL (*C. N.*, viii., 38).—Titrate hot AmHO solution with  $\text{Na}_2\text{S}$ , using freshly precipitated ZnS as indicator. Ni or Zn do not interfere. JEAN (*C. N.*, lxxvii., 172) uses  $\text{PbCO}_3$  paper as indicator ; the process separates As. BORNTÄGER (*J. C. S.*, lxvi., ii., 120) uses a ferro-cyanide indicator, and says Cu-Zn alloys may be thus titrated.
1706. CASAMAJOR (*C. N.*, xlv., 167).—Titration of AmHO solutions as in 1705 until blue colour goes is inaccurate. Precipitates instead from alkaline tartrate solutions until no further cloud forms. Same process for Pb, etc.
1707. BALLING (*C. N.*, xlvii., 248).—The sulphide of Cu (Pb, Zn, or Hg) is digested with  $\text{AgNO}_3$  and excess Ag titrated with KCNS.
1708. LUCKOW (*J. C. S.*, lxiv., ii., 242).—Titration of Cu-Sn-Sb alloys with ferro-cyanide. RANTER (*J. C. S.*, lxx., i., 3).—The precipitate always retains  $\text{K}_4\text{Fe}(\text{CN})_6$ . SPICA (*J. C. S.*, lxx., ii., 127) uses  $\text{Fe}_2\text{Cl}_6$  indicator. (See also 1581.)

1709. QUESSAND (*J. C. S.*, xlviii., 441).—Precipitate with slight excess of  $K_4Fe(CN)_6$ , and then measure the alkaline solution of Rochelle salt needed to destroy the precipitate.
- 1710 DONATH and HATTENSAUR (*J. S. C. I.*, 1890, 554). — Cu precipitated with ferro-cyanide from alkaline tartrate solutions. Fe should be present, so that end-reaction (blue) may be noted by adding acetic acid to test drop.
1711. BERNTHSEN (*C. N.*, xliii., 79).—Titrate cupric solution with hypo. in an atmosphere of H. When colour is nearly gone add indigo to heighten end-reaction.
1712. LAGRANGE (*C. N.*, xxx., 241).—Precipitate with KHO, convert to tartrate, and reduce to  $Cu_2O$  with standard glucose.
1713. MULLER (*C. N.*, xxxi., 143).—Measure volume of H needed to reduce  $CuO$  to Cu in a closed tube.
1714. VITALI (*J. C. S.*, lxviii., ii., 140).—Mix  $CuSO_4$  with KI and starch, add  $H_2SO_3$  to decolourize, and estimate liberated  $H_2SO_4$  with standard alkali.
1715. ETARD and LEBEAU (*C. N.*, lxi., 137).—Add hydrobromic acid to concentrated solution, and then standard  $SnCl_2$  until the violet colouration is discharged.
1716. PURGOTTI (*J. C. S.*, lxxii., ii., 349).—Boil solution with excess NaCl and hydrazine sulphate. The evolved N is measured at normal temperature and pressure.
1717. LESCŒUR (*J. C. S.*, lxxiv., ii., 484).—Cu is precipitated as oxide, dissolved in excess acid and titrated back with alkali.  $Cu_2O$  obtained with glucose titrated similarly. See also RUOSS (*J. C. S.*, lxxiv., ii., 644).

#### IV. Colorimetric Estimations.

1718. CARNELLEY (*C. N.*, xxxii., 308).—The colour formed with ferro-cyanide in neutral solution is compared with standards.  $AmNO_3$ , etc., heighten the colour. Many alkaline and earthy salts do not interfere. Detects (so does  $H_2S$ ) 1 part in 1,500,000. See also ILES (*C. N.*, xxxiv., 16) and BLUNT (*C. N.*, xxxiii., 7).
1719. LUCAS (*C. N.*, lxxix., 67).—Process 1718 used for estimating O in Cu and Cu in Fe. Separation of Fe and Cu not complete after several re-precipitations with  $AmHO$ .
1720. MUIR (*C. N.*, xxxiii., 11).—Add  $H_2S$  and compare with standards. Determines minimum and maximum which can be estimated thus.
1721. HEATH (*C. N.*, lxxvi., 184).—Comparison of  $AmHO$  solutions. Permanent standards prepared from  $CuSO_4$ . (See 1647.)

#### V. Detection.

1722. BELLAMY (*C. N.*, xx., 228).—An alcoholic tincture of campeachy wood detects 1 part Cu (or Fe) in 20,000,000 parts of water.

1723. WAGNER (*C. N.*, xlv., 35).—Limits of following tests are: Ferrocyanide, 1 in 200,000; AmHO, 1 in 25,600; xanthogenate, 1 in 900,000.
1724. ALIAMET (*C. N.*, lvi., 160).—Pyrogallie acid in saturated  $\text{Na}_2\text{SO}_3$  gives red colour with Cu. (*C. N.*, lviii., 293).—Test by no means characteristic.
1725. CAILLETET (*C. N.*, xli., 160).—Add pyrogallie acid in ether to the oil; a brown colour = Cu.
1726. ANON. (*C. N.*, xliii., 117).—One one-hundredth m.grm. Cu can be detected by the HBr test.
1727. DENIGES (*C. N.*, lix., 168; and *J. C. S.*, lxxviii., ii., 330).—A more stable form of reagent for above test is saturated KBr in  $\text{H}_2\text{SO}_4$ .
1728. SABATIER (*J. S. C. I.*, 1894, 1092).—KBr and  $\text{H}_3\text{PO}_4$  may be used instead of HBr. Detects one-tenth m.grm. Cu.
1729. KERN (*C. N.*, xxxiv., 78).—Precipitate acid solution of iron with AmHO, acidify evaporated filtrate, and add Mg. Traces of precipitated Cu observed with the microscope.
1730. WOODCOCK (*C. N.*, xxxvi., 240).—Precipitate Cu with Zn-Pt element; expose Pt to Br + HBr; the violet colour detects 0.001 m.grm. Cu.
1731. JAWOROWSKY (*J. C. S.*, lxxii., ii., 285).—Shake AmHO solution with phenol; with traces of Cu, solution becomes turbid and blue.
1732. BACH (*J. S. C. I.*, 1899, 401).—Mixture of formaldehyde and hydroxylamine hydrochloride gives violet colour with one part Cu in a million.
1733. CAZENEUVE (*J. C. S.*, lxxviii., ii., 627).—Diphenyl-carbazide in benzene gives a violet colour when shaken with a cupric solution.
1734. LENOBLE (*J. C. S.*, lxiv., 554).—Potassium mercuric iodide throws down bright red precipitate from cupric solutions.
1735. THOMS (*C. N.* lxiv., 190).—Depends on yellow colour formed with KI. One part in 200,000. (See 1688).
1736. GERLAND (*C. N.*, ix., 73) and CHAPMAN (*C. N.*, xii., 231).—Blowpipe test for Cu.
1737. SCHIFF (*C. N.*, i., 191) and ORLOWSKI (*C. N.*, xlvii., 24).—Tests for cuprous oxide.

## VI. Miscellaneous.

1738. THOMSEN (*C. N.*, xxxix., 185).—Precipitate formed with  $\text{H}_2\text{S}$  is not  $\text{CuS}$ , but a mixture of S and a lower sulphide. See also COPPOCK (*C. N.*, lxxiii., 262; and lxxvi., 231) and BRAUNER (*C. N.*, lxxiv., 99).
1739. ANON. (*C. N.*, xlvi., 120).— $\text{Cu}(\text{NO}_3)_2$  mixed with  $\text{Pb}\bar{\text{A}}_2$  is dissolved by NaHO and not re-precipitated on boiling. (See 970.)
1740. DEBRAY (*C. N.*, xlvii., 304).— $\text{CuS}$  is dissolved in considerable quantities by  $\text{Am}_2\text{S}$  if Mo is also present.

The following refer to papers which deal generally with the estimation of the impurities of commercial copper :

1741. ABEL and FIELD (*C. N.*, iv., 264); ABEL (*C. N.*, ix., 124) ; FRESNIUS (*C. N.*, xlvii., 18) ; KUHN (*J. S. C. I.*, 1884, 374) ; JEAN (*J. S. C. I.*, 1896, 677) ; HAMPE (*J. S. C. I.*, 1894, 421 ; and 1897, 1043) ; KELLER (*J. C. S.* lxxviii., ii., 186) ; WARREN (*C. N.*, lv., 62 ; and lxxiii., 37) ; BENNEVILLE (*J. C. S.*, lxvi., ii., 297 and 298) ; MURMAN (*J. C. S.*, lxxii., ii., 346) ; HOLLARD (*J. S. C. I.*, 1897, 166 and 763 ; and *C. N.*, lxxxi., 258), electrolytic ; CLARK (*J. S. C. I.*, 1900, 27) ; ULKE (*J. S. C. I.*, 1900, 170) ; TRUCHOT (*J. S. C. I.*, 1901, 283).

The following deal with the estimation of As in Cu :

1742. CLARKE (*J. S. C. I.*, 1887, 353) ; PLATTEN (*J. S. C. I.*, 1894, 324) ; PATTINSON (*C. N.*, xlv., 136) ; HEATH (*J. S. C. I.*, 1897, 699) ; GIBBS (*J. S. C. I.*, 1901, 184).

The following deal with the estimation of O in Cu :

1743. AUBEL (*C. N.*, xix., 238) ; SABATIER (*J. C. S.*, lxxii., ii., 261) ; ANON. (*C. N.*, xxxvi., 241) ; LUCAS (*C. N.*, lxxx., 86, and *J. S. C. I.*, 1891, 157) ; DEWEY (*J. S. C. I.*, 1889, 134) ; BLOUNT (*J. S. C. I.*, 1896, 296) ; ARCHBUTT (*J. S. C. I.*, 1900, 1148). The estimation of O is also dealt with in many papers under 1741.
1744. WHITEHEAD (*J. S. C. I.*, 1895, 513).—Fe in Cu.
1745. SMITH (*C. N.*, lxxii., 76) and GODSHALL (*J. C. S.*, lxxx., ii., 42).—Au and Ag in copper. (See also 1685.)

## IRON.

The classification is :

- I. SEPARATIONS FROM OTHER METALS.
- II. GRAVIMETRIC ESTIMATIONS.
- III. VOLUMETRIC ESTIMATIONS.
  - a. As Ferrous Salts.
  - b. As Ferric Salts.
- IV. COLORIMETRIC ESTIMATIONS.
- V. MISCELLANEOUS NOTES.

### I. Separations from other Metals.

*Lime and Magnesia :*

1746. ROSE (*C. N.*, ii., 291).—Add AmHO ; any CaCO<sub>3</sub> formed is decomposed on boiling if AmHO salts are present.

1747. CALVERT (*C. N.*, ii., 328).—CaO is not separated with AmHO. Precipitate neutralized iron solution as basic succinate.
1748. GIBBS (*C. N.*, xi., 102).—Fe and Al are separated as acetate from Ca, Mg, Zn, and Ur.
1749. GUYARD (*C. N.*, xlix., 259).—Keeping Fe, Al, etc., in solution as citrate, Ca may be precipitated as oxalate and Mg as phosphate.

*Uranium.* (See also 1748.)

1750. PISANI (*C. N.*, iii., 257).—Precipitate Fe with  $\text{Am}_2\text{CO}_3$  and separate the little Fe in the filtrate with  $\text{Am}_2\text{S}$ .
1751. BURKER (*C. N.*, xxxviii., 276).—Process 1750 inaccurate. Precipitate with AmHO, weigh, reduce in H, and dissolve out the Fe with HCl. (See 966.)
1752. WALKER (*J. C. S.*, lxxiv., ii., 540).—Pour acid mixture into NaHO +  $\text{H}_2\text{O}_2$ ; U in the filtrate. RHEINECK (*C. N.*, xxiv., 233).—Proceeds as 1748.
1753. CLASSEN (*J. C. S.*, xlviii., 192).—Fe deposited from solution containing large excess of oxalate leaves U in solution.

*Beryllium:*

1754. SCHLEIER (*J. S. C. I.*, 1892, 713) and ATKINSON and SMITH (*J. C. S.*, lxx., ii., 220).—Fe precipitated with nitroso- $\beta$ -naphthol.
1755. HAVENS and WAY (*C. N.*, lxxx., 285).—Be, Cr, and Zr are separated as in 1517.

*Arsenic.* (See 786 *et seq.*)

1756. JANNASCH and KAMMERER (*J. C. S.*, lxx., ii., 221).—Pour HCl solution into NaHO +  $\text{H}_2\text{O}_2$ ; As in solution.

*Cadmium:*

1757. STORTENBECKER (*C. N.*, lxxx., 16).—The Fe is converted to ferro-cyanide and the Cd electro-deposited.

*Zirconium:*

1758. MATTHEWS (*C. N.*, lxxix., 97).—Method based on insolubility of oxy-chloride of Zr, etc., in ether. Ce, Ti, etc., are similarly separated. Résumé of methods for separating Fe and Zr.

*Thallium:*

1759. CROOKES (*C. N.*, vii., 194).—Reduce to FeO with hypo. and precipitate Tl with KI. Indicates 0.0002 grm.

*Cerium.* (See also 1758.)

1760. GIBBS (*C. N.*, x., 195).—Add saturated  $\text{Na}_2\text{SO}_4$ . Ce, La, Dy are precipitated; Fe, Al, Gl, Yt, and Ur are in solution.

## II. Gravimetric Estimations.

1761. FRESSENIUS (*C. N.*, iv., 150).— $\text{Am}_2\text{S}$  precipitates Fe slowly, but completely; AmCl assists; AmHO not harmful; ferric salts imperfectly precipitated.

1762. BLUM (*J. S. C. I.*, 1888, 456).—Mix with tartaric acid, precipitate with  $\text{Am}_2\text{S}$ , dissolve in  $\text{HCl}$ , precipitate with  $\text{AmHO}$ , and weigh as  $\text{Fe}_2\text{O}_3$ .
1763. KONINCK (*C. N.*, lxii., 19) and MEINECKE (*J. S. C. I.*, 1888, 237).—Precipitate neutralized solution with nitroso- $\beta$ -naphthol and ignite to  $\text{Fe}_2\text{O}_3$ . Al is separated, but not Cu, Co, and P.
1764. CROSS (*C. N.*, xxxvii., 26).—Extent of error introduced by precipitating  $\text{Fe}_2(\text{HO})_6$  in the presence of salts of the alkalis and alkaline earths.
1765. MEUNIER (*C. N.*, xx., 264).—Powdered meteoric stones digested with  $\text{AuCl}_3$ . Amount of Au deposited is estimated.
1766. KRUG (*C. N.*, lxxv., 69).—Résumé of methods for estimation of Fe (and Al) in the presence of  $\text{P}_2\text{O}_5$ . The following refer mainly to the valuation of agricultural products:—OGILVIE (*C. N.*, xxv., 277); DYER (*C. N.*, liii., 51); JONES (*C. N.*, liii., 87; and lxxv., 234); MELLOX (*C. N.*, liii., 85); GLASER (*C. N.*, lxi., 181); GRÜBER (*C. N.*, lxiii., 146); PELLET (*C. N.*, xxxv., 268); VINCENT (*C. N.*, lxx., 297); GLADDING (*C. N.*, lxxiv., 112 and 146); BLATTNER and BRASSEUR (*C. N.*, lxxvi., 150); LINDET (*C. N.*, lxxvi., 212); and many others.

The following refer to electrolytic depositions:

1767. SMITH (*J. S. C. I.*, 1888, 693), Al and Ti do not interfere; BRAND (*J. S. C. I.*, 1889, 1011); RUDORFF (*J. C. S.*, lxiv., ii., 93); HEIDENREICH (*J. S. C. I.*, 1896, 744); NICHOLSON and AVERY (*C. N.*, lxxiv., 91); and AVERY and DALES (*J. S. C. I.*, 1899, 300 and 610).

### III. Volumetric Estimations.

#### a. As Ferrous Salts:

1768. BLUNT (*C. N.*, viii., 54).—Very dilute solutions of  $\text{HCl}$  decompose permanganate. Rate of decoloration observed.
1769. ZIMMERMAN (*C. N.*, xlvi., 12).—Presence of  $\text{MnO}$  salts prevents perturbing action of  $\text{HCl}$  in  $\text{KMnO}_4$  titrations. See also KRUTWIG (*C. N.*, xlviii., 102); THOMAS (*C. N.*, xlviii., 119) uses lead chloride for the same purpose; HOOD (*C. N.*, l., 278) uses  $\text{MgSO}_4$  or  $\text{Am}_2\text{SO}_4$ ; LUKE (*C. N.*, lviii., 186), sulphates of Ca, Co, and Mg have no value in this respect. (See 1789.)
1770. MOYANCE (*C. N.*, xx., 45).—Reduction to  $\text{FeO}$  best effected by amalgamated Zn. Best means of making  $\text{KMnO}_4$  estimation stated.
1771. KOPP (*C. N.*, xxix., 242).—Uses  $\text{SnCl}_2$  to accelerate the reduction by Zn.
1772. BEEBE (*C. N.*, liii., 269).—Suspends the amalgamated Zn in a Pt basket.
1773. MORGAN (*J. S. C. I.*, 1901, 143).—Effects reduction with a zinc copper couple.
1774. EBELING (*J. C. S.*, lxxx., ii., 424 and 580).—Boil with Zn in the presence of  $\text{KCNS}$  to disappearance of red colour. VOLHARD says the use of sulpho-cyanide is misleading and erroneous.



1775. DONATH and JELLER (*C. N.*, liv., 73).—Mix ignited  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  with Zn powder, heat, dissolve iron in  $\text{H}_2\text{SO}_4$ , and titrate. Process separates Fe from Al and Cr. JUPTNER (*J. I. S. I.*, 1894, ii., 497).—Uses Mg instead of Zn for ores, slags, etc.
1776. CARNEGIE (*J. C. S.*, liii., 468).—Reduces by filtering through Zn dust. JONES (*C. N.*, lx., 93).—Filters through pulverized Zn and illustrates its many advantages. See also SHIMER (*J. C. S.*, lxxviii., ii., 50).
1777. MACIVOR (*C. N.*, xxix., 246).—Hæmatites readily dissolve as FeO on heating with  $\text{H}_2\text{SO}_4$  and Zn, and so avoid HCl in the  $\text{KMnO}_4$  titration.
1778. SCHMIDT (*C. N.*, xlviii., 245).—Zn used to form FeO interferes with ferro-cyanide indicator.  $\text{SnCl}_2$  recommended.
1779. STORCH (*J. S. C. I.*, 1893, 866).—Reduce to FeO with Cu, and titrate with  $\text{KMnO}_4$ . Ignited  $\text{Fe}_2\text{O}_3$  is soluble in 40 per cent.  $\text{H}_2\text{SO}_4$ .
1780. HART (*C. N.*, xxxiv., 65).—Reduce ore to metal in H, dissolve in  $\text{H}_2\text{SO}_4$ , and titrate with  $\text{KMnO}_4$ . Or, dissolve in HCl, add excess  $\text{SnCl}_2$ , and go back with I. MOISSAN (*C. N.*, xl., 89).—After heating in H, Fe may contain FeO and  $\text{Fe}_3\text{O}_4$ .
1781. REYNOLDS (*C. N.*, x., 228).— $\text{H}_2\text{S}$  is a better reagent for forming FeO than either Zn or  $\text{SO}_2$ .
1782. ESILMANN (*C. N.*, xxviii., 208).—Reduces  $\text{Fe}_2\text{O}_3$  with  $\text{Am}_2\text{S}$ .
1783. LINOSSIER (*C. N.*, li., 179).—Reduce with  $\text{H}_2\text{S}$ , destroy last traces by adding  $\text{HgCl}_2$ , and titrate with  $\text{KMnO}_4$ .
1784. WELLS and MITCHELL (*C. N.*, lxxiii., 123).—Reduce with  $\text{H}_2\text{S}$ ; precipitated S no effect on  $\text{KMnO}_4$  titration. Cu removed by filtration.
1785. AUSTEN and HURFF (*C. N.*, xlvi., 287).—Résumé of  $\text{Fe}_2\text{O}_3$  to FeO reductions; recommends  $\text{Na}_2\text{SO}_3$ . Boil until steam no longer decolourizes  $\text{KMnO}_4$ . REINSCH (*C. N.*, v., 126).—Cu wire by a brown colouration on its surface will detect one-millionth part  $\text{SO}_2$ . BROWN (*J. C. S.*, liv., 267).—Tests for  $\text{SO}_2$  by paper soaked in ferric chloride and ferri-cyanide.
1786. ATKINSON (*C. N.*, xlix., 117).—Bisulphite added to neutral solution best means of forming FeO. Errors due to Zn and  $\text{SnCl}_2$ . Speed of ferri-cyanide indicator and rate of decomposition.
1787. CLARKE (*C. N.*, xvii., 234).—Fuse ore, slag, or cinder with bisulphate and cryolite, dissolve in HCl, reduce, and titrate with  $\text{K}_2\text{Cr}_2\text{O}_7$ .
1788. REINHARDT (*J. I. S. I.*, 1885, 299; 1889, i., 400; and 1900, i., 375).—Add  $\text{SnCl}_2$  to hot acid  $\text{Fe}_2\text{Cl}_6$ , destroy excess with  $\text{HgCl}_2$ , add  $\text{MnSO}_4$ , and then  $\text{H}_3\text{PO}_4$ , so that  $\text{Fe}_2\text{Cl}_6$  colour may not mask  $\text{KMnO}_4$  end-reaction. See also BYA (*C. N.*, lvi., 279); and MITCHELL (*J. S. C. I.*, 1894, 1096).
1789. CADY and RUDIGER (*J. I. S. I.*, 1897, ii., 508).— $\text{SnCl}_2$  reduction; accurate  $\text{KMnO}_4$  titration in the presence of  $\text{HgSO}_4$ .
1790. NAMIAS (*J. I. S. I.*, 1892, i., 492).—Add excess  $\text{K}_2\text{Cr}_2\text{O}_7$  to FeO solution, and a few drops of I and starch, and titrate with  $\text{SnCl}_2$ .
1791. MIXER and DUBOIS (*J. I. S. I.*, 1895, ii., 601).—Dissolve ore in HCl +  $\text{SnCl}_2$ , destroy excess  $\text{SnCl}_2$  with  $\text{HgCl}_2$ , and titrate with  $\text{KMnO}_4$ .

1792. MAHON (*J. I. S. I.*, 1894, i., 617).—Pt carried by fusion flux into solution is reduced by  $\text{SnCl}_2$ , and leads to error.
1793. MITTENZWAY (*C. N.*, ix., 253).—Measure O absorbed by alkaline FeO solution by weighing the water which runs into closed operating bottle.
1794. ROSS (*J. C. S.*, lxxii., ii., 193).—Add  $\text{K}_2\text{Cr}_2\text{O}_7$  to FeO solution, and determine the excess by Baumann's process (1050).
1795. PARKER (*C. N.*, xxii., 313).—Cu interferes with ferro-cyanide indicator. Reduction of  $\text{Fe}_2\text{O}_3$  with Zn would remove all the Cu.
1796. HOGG (*C. N.*, lix., 207).—Cu in Fe alloys is not dissolved by dilute acids (see 1643) and reduces  $\text{Fe}_2\text{O}_3$  as it is formed in the titration. Dissolve in  $\text{HCl} + \text{KClO}_3$ , and reduce with  $\text{SO}_2$ .
1797. RIDEAL and ROSENBLUM (*J. S. C. I.*, 1896, 158).—Nickel gives a brown colour with ferro-cyanide, which may mask the end-reaction with dilute FeO solutions. JERVIS (*C. N.*, lxxvii., 133).—Mn acts similarly.
1798. BLUM (*J. I. S. I.*, 1900, ii., 582).—The almost unfailing presence of V in tap cinder interferes with volumetric determinations; gives elaborate gravimetric method.
1799. ATKINSON (*C. N.*, xlix., 117).—Means of standardizing  $\text{K}_2\text{Cr}_2\text{O}_7$ . The C in steel used for the purpose leads to low results. (See 435.)
1800. WELLBORN (*C. N.*, xx., 57).— $\text{FeSO}_4$  is preserved from oxidation by placing camphor (in paper) therewith. GAWALOWSKI (*C. N.*, xlvii., 165) uses pyrogallie acid similarly.
1801. VOGEL (*C. N.*, xxiii., 142).—An exposure to direct sunlight for thirty seconds may cause ferri-cyanide to give a blue colour with ferric salts.
1802. STOCK (*C. N.*, xxxix., 47).—A simple apparatus for effecting reductions out of contact with air.
1803. JOHNSON (*C. N.*, xlv., 287).—FeO solutions are oxidized the more readily if external air is excluded; suggests that  $\text{FeSO}_4$  has ozonizing action on enclosed air.
1804. PATTINSON (*C. N.*, xxi., 268).—Hot  $\text{FeSO}_4$  solutions exposed to the air to cool are not appreciably, if at all, oxidized.
1805. WILLBUR and WHITTLESEY (*C. N.*, xxii., 2).—Mix powdered silicate with  $\text{CaF}_2 + \text{HCl}$ , heat in coal-gas, and titrate FeO with  $\text{KMnO}_4$ . ALLEN (*C. N.*, xxii., 57).—Estimates FeO by digesting ore or sand in closed tube with  $\text{HCl}$ .
1806. EARLEY (*C. N.*, xxx., 169) and DÖLTER (*C. N.*, xxxix., 135).—Decomposes silicate with  $\text{HF}$ , and titrates with  $\text{KMnO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7$ .
1807. PRATT (*J. C. S.*, lxvi., 482).—Dissolves silicate in  $\text{HF} + \text{H}_2\text{SO}_4$  in  $\text{CO}_2$  in a Rose's crucible.
1808. CHESTER and CAIRNS (*J. C. S.*, liv., 196).—Use  $\text{AmF} + \text{H}_2\text{SO}_4$  in  $\text{CO}_2$  atmosphere.
1809. PENFIELD and FOOTE (*J. C. S.*, lxxvi., ii., 305).—Determine FeO in tourmaline by fusing with borax in an inert atmosphere and titrating  $\text{H}_2\text{SO}_4$  solution with  $\text{KMnO}_4$ .

1810. HILLEBRAND (*C. N.*, lxxxii., 211).—Comparison of sealed tube and HF methods of estimating FeO; the former often too high. (See also *C. N.*, lxxviii., 106.)
1811. NEUMANN (*J. S. C. I.*, 1887, 680).—Metallic Fe in slag, etc., is estimated by treating with acid and collecting the H evolved in a modified Lunge nitrometer.

*b. As Ferric Salts:*

1812. LANDOLT (*C. N.*, vi., 184).—Destroy free HCl with  $\text{Na}\bar{\text{A}}$ , add excess hypo., and titrate with I and starch.
1813. CRAFTS (*C. N.*, xxviii., 44).—Evaporate HCl solution until the crust on the surface dissolves with difficulty; titrate with hypo.
1814. OUDEMANN (*C. N.*, xvi., 218; and xxii., 256).—To HCl solution add KCNS and titrate with hypo. Sr, Ca, Mg, Mn, Ni, Co, and Cu do not interfere.
1815. HASWELL (*J. I. S. I.*, 1883, 385).—Add sodium salicylate in 1814; then hypo. till violet colour goes, and then  $\text{K}_2\text{Cr}_2\text{O}_7$  till it reappears. See also OUDEMANN and HASWELL (*C. N.*, xlvii., 210) and BRUEL (*C. N.*, xlviii., 248).
1816. NORTON (*C. N.*, lxxx., 89).—Estimation with hypo. and I. Determines some necessary relations between acidity, dilution, etc.
1817. PSZCZOLKA (*C. N.*, xlvii., 107) and PARTHIEL (*J. I. S. I.*, 1890, i., 374).—Add KI to faintly acid ferric solution, and titrate with hypo. and starch.
1818. FALIERES (*J. C. S.*, xlviii., 1011) and NIHOUL (*C. N.*, lxvii., 196).—Distil acidified  $\text{Fe}_2\text{Cl}_6$  with KI, and titrate volatilized iodine.
1819. CARNEGIE (*C. N.*, lx., 87).—Investigates nature of reaction between  $\text{Fe}_2\text{Cl}_6$  and KI, on which estimation of former depends.
1820. MORELLS (*J. S. C. I.*, 1884, 179).—Heat with KI, add a known amount of Hg, and shake. The free I and Hg combine and the Fe is deduced from the loss of Hg on re-weighing.
1821. WINKLER (*C. N.*, xxi., 233).—Add KCNS and then CuCl until the colour disappears and a cloud of CuCNS is formed. Co, Ni, Cu, and As do not interfere. See also GIBBS (*C. N.*, xvii., 161).
1822. WEIL (*C. N.*, xlvi., 284) and JEAN (*J. C. S.*, lxiv., ii., 492).—Add  $\text{SnCl}_2$  to HCl solution of  $\text{Fe}_2\text{Cl}_6$  until colour goes; or add  $\text{CuCl}_2$  to heighten end-reaction.
1823. HEMPEL (*C. N.*, lii., 321).—Ignite with  $\text{Na}_2\text{CO}_3 + \text{CaCO}_3$  to eliminate organic matter, dissolve in HCl, and titrate with  $\text{SnCl}_2$ .
1824. MAHON (*J. S. C. I.*, 1893, 1061).— $\text{SnCl}_2$  is added to a solution containing  $\text{HgCl}_2$  and a little  $\text{PtCl}_4$ ; a faint excess precipitates a dark cloud of finely-divided Hg and Pt.
1825. ZENGELIS (*J. S. C. I.*, 1901, 840).—Add  $\text{SnCl}_2$  to boiling solution; a faint excess in contact with a molybdate solution shows a blue colour.
1826. MORAHT (*C. N.*, lxv., 275).—Add ferro-cyanide until the sulpho-cyanide colour, kept in solution with ether, is dispersed.

1827. CHARPENTIER (*C. N.*, xxviii., 71).—To solution containing no free and add KCNS and titrate with caustic alkali. A like process was suggested by Ross (*C. N.*, xvii., 23 and 35) and adversely criticised by WRIGHT.
1828. PURGOTTI (*J. C. S.*, lxxii., ii., 77).—An acid solution of the blue oxide ( $\text{Mo}_3\text{O}_8$ ) mixed with hot  $\text{Fe}_2\text{O}_3$  solutions is quantitatively decolourized.
1829. JUETTE (*C. N.*, xvii., 63).—The amount of tartaric acid needed to retain iron (Cr, Mn, Al) in solution is proportional to the amount of the latter.
1830. CARNOT (*J. S. C. I.*, 1889, 138).—Cold acid FeO solutions are more effectually oxidized by  $\text{H}_2\text{O}_2$  than by any other reagent.

#### IV. Colorimetric Estimations.

1831. DAVIES (*C. N.*, viii., 163).—Add KCNS, and compare with standard.
1832. SKEY (*C. N.*, xvi., 180 and 233).—When the mixed  $\text{Fe}_2\text{Cl}_6$  and KCNS is treated with excess HCl, Fe is volatilized at ordinary temperatures.
1833. KRÜSS and MORAHT (*C. N.*, lxiv., 255).—The KCNS colour is due to the formation of  $\text{Fe}(\text{CNS})_3 \cdot 9\text{KCNS} + 4\text{H}_2\text{O}$ .
1834. LUNGE (*C. N.*, lxxiii., 250).—Shakes out the KCNS colour with ether. Better to oxidize Fe with  $\text{KClO}_3$  than with  $\text{HNO}_3$ .
1835. WEBER (*C. N.*, xlvii., 165).—Chlorides of the alkaline earths retard or may prevent the KCNS reaction.
1836. THOMSON (*C. N.*, li., 259).—Ag, Cu, Co, and  $\text{HgCl}_2$  interfere with the KCNS colour.
1837. TATLOCK (*J. S. C. I.*, 1887, 276).—Influence of reagents, free acid, oxidizers, etc., on the KCNS colour.
1838. VERNON (*C. N.*, lxvi., 177, etc.).—Influence of temperature, dilution, acidity, etc., on the KCNS test. See also GLADSTONE (*C. N.*, lxvii., 1 and 66); ANDREWS (*C. N.*, lxx., 165); KRÜSS and MORAHT (*C. N.*, lxvi., 198); and RIBAN (*J. S. C. I.*, 1892, 269).
1839. SABANEEFF (*J. C. S.*, liv., 757).—Colour of  $\text{Am}_2\text{S}$  solutions used.
1840. JOB (*J. C. S.*, lxxvi., ii., 51).—FeS dissolved in sodium pyrophosphate gives a green solution well adapted to a colorimetric estimation of Fe.
1841. CARNELLEY (*C. N.*, xxx., 257).—The blue colour formed by ferrocyanide can detect 1 part Fe in 13,000,000 of water. Process elaborated for estimation of Fe in water.
1842. WAGNER (*C. N.*, xlv., 35).—Limit of sensitiveness of some reactions for Fe and Cu. (See also 1722.)

#### V. Miscellaneous.

1843. JULIEN (*C. N.*, xxiv., 292), BLAIR (*C. N.*, lvi., 183), and MORGAN (*J. S. C. I.*, 1894, 1023).—Schemes for elaborate analysis of iron ores.
1844. BETTEL (*C. N.*, xliii., 100).—Discusses the determination of basic cinder and oxides in iron, and reviews a number of methods proposed for

this purpose. The following (not exhaustive) references are to papers dealing with the estimation of oxides or slag:—GLADKY (*J. C. S.*, lxiv., ii., 388); PARRY and MORGAN (*C. N.*, lxvii., 260); LEDEBUR (*J. S. C. I.*, 1882, 366); SCHNEIDER (*J. S. C. I.*, 1900, 693); TUCKER (*J. I. S. I.*, 1881, 205).

1845. FOEHR (*C. N.*, xlvi., 40).—Ores containing  $\text{MnO}_2$  need prolonged boiling to expel the Cl formed, and  $\text{Fe}_2\text{Cl}_6$  is volatile even at  $50^\circ$ .
1846. FRESENIUS (*C. N.*, xvi., 37) and TALBOT (*C. N.*, lxxv., 227).— $\text{Fe}_2\text{Cl}_6$  is not volatilized on boiling with acids.
1847. BORNTRÄGER (*J. C. S.*, lxx., ii., 502; and lxxviii., ii., 171).—Ignited  $\text{Fe}_2\text{O}_3$  dissolves instantly if metallic iron is also being dissolved in the HCl, or if a little  $\text{MnO}_2$  is added.
1848. ANON. (*C. N.*, xxxviii., 11).—Ignited  $\text{Fe}_2\text{O}_3$  can be dissolved in HCl after boiling to flocculent condition with KHO.
1849. ZIRNITE (*J. I. S. I.*, 1888, i., 368).—A 30 per cent. NaHO solution dissolves  $\text{Fe}_2\text{O}_3$  as  $\text{NaFeO}_4$ ; it is re-precipitated on diluting or standing.
1850. JEANNEL (*C. N.*, xvii., 286).—Properties of “neutralized” ferric chloride [ $\text{Fe}_2\text{Cl}_6 \cdot 9\text{Fe}_2(\text{HO})_6$ ] solutions.
1851. WARREN (*C. N.*, lxxii., 100).—Au and Ag were estimated in iron by making the sample (4 lbs.) the + pole of an acid battery. The C residue and a little Fe were mixed with litharge, cupelled, etc.
1852. WARREN (*C. N.*, lxxv., 91).—Samples which have been in contact with a borax flux contain B up to 2 per cent.
1853. WIBORGH (*C. N.*, lxxviii., 4).—Determines the reducibility of Fe ores. The reduced Fe is estimated by measuring the H evolved on treating with acids.
1854. MEUNIER (*C. N.*, xix., 5).—Immediate analysis of meteoric iron.
1855. LEDEBUR (*J. I. S. I.*, 1894, ii., 483).—Uses the ether method to separate iron from Cu, Sb, As, Pb, Cr, V, Mn, Ni, Co, and Ti existing in steel.
1856. J. T. (*C. N.*, lxxix., 157).—Insoluble specular ores are mixed with ashless filter-paper and ignited; they are then soluble in HCl.
1857. BECHAMP and SAINTPIERRE (*C. N.*, iv., 316).—Metallic Pt reduces HCl solutions of  $\text{Fe}_2\text{Cl}_6$ , and is itself dissolved thereby.
1858. DUDLEY (*C. N.*, lxxv., 257).—“Some Present Possibilities in the Analysis of Iron and Steel.”

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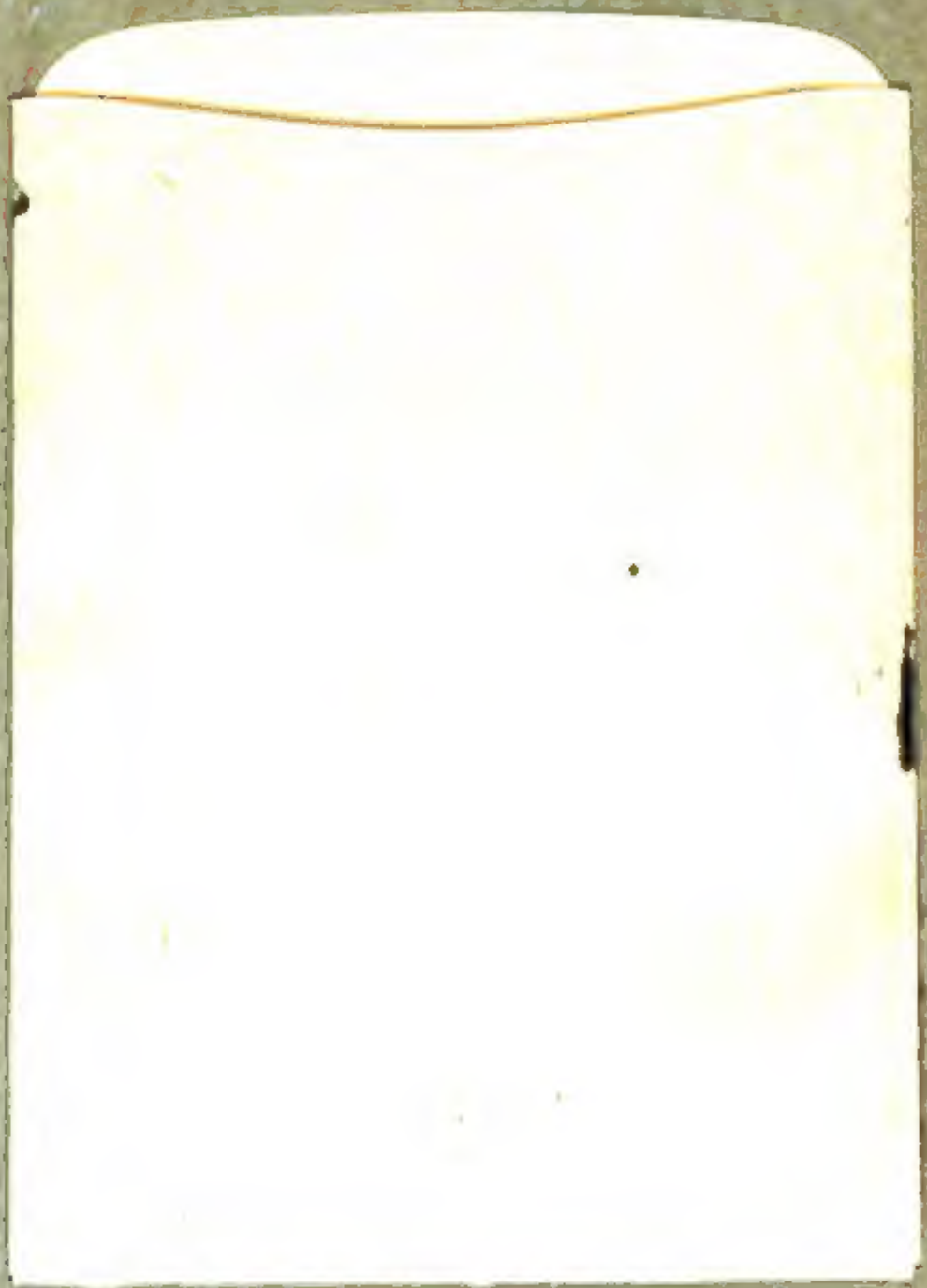
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